

Document Title

Summary of the residues in or on treated products, food and feed for

Data Requirements 7/2009 & EU Regulation EU Regulation 1107/2009 & EU Regulation 283/201 Section 6: Residues in or on treated products, food and feed

Data Requirements

Julation 1107/2009 & EU Regulation

Document MCA

a 6: Residues in or on treated products, food

According to the guidance document SANCO 10181/2013 for preparing dossers for the approval of schemical active substance.

Date

2017-07-24



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Version history

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INTRODUCTION

Ethephon is a plant growth regulator and was included into Annex I of Directive 91/414 in 2006 (Directive 2006/85/EC, dated 23rd of October 2006, Entry into Force 1st of August 2007).

This dossier contains only summaries of studies, which were not available at the time of the first Annex I inclusion of ethephon and were, therefore, not evaluated during the first EU review of this compound. All other studies, which were already submitted by Bayer AC formerly Bayer CropScience AG for the first Annex I inclusion, are contained in the Monograph and in the baseline dossier (D-012067-01). Where applicable, such studies are indicated by grey typeface in the summary dossier(s).

The here presented and submitted studies used different synonyms and codes for the active substance ethephon, its metabolites and reference compounds. In order to present a common basis for the evaluation the following list summarizes all names used.

Formula Report name used in summaries Codes used 16 PAC index name / Other names codes.

Formula	Colles used V V V
Report name used in summaries	DPAC index name / Other names / codes
Ethephon	AE F@6382
	Ethephon technical concentrate
	Ethephon Base 250
Ethephon-2-hepa	HEPA, 2-HEPA
	(2 drydroxyethyl)phosphonie acid

In addition, a list of metabolites, which contains the structure. The synonyms and code numbers attributed to the compound is presented in Document N3 of this dossier. The matrices in which the metabolites were identified are also included in this list.



CA 6 RESIDUES IN OR ON TREATED PRODUCTS, FOOD AND FEED

The active substance ethephon (2-chloroethylphosphonic acid) is a plant growth regulator which acts in plants by releasing ethylene. It is used on various crops, e.g. to control flowering (fruit trees), increase resistance to lodging (cereals), promote maturation and coloration (topatoes, apples), or facilitate harvest (cotton).

An Annex II Dossier for the inclusion of Ethephon in the Annex I of Directive 90414 was submitted to EU authorities in April 2002. After in-depth evaluation of the data, the Netherland pacting as Rapporteur Member State) issued a Draft Assessment Report in June 2004. This report served as the basis for the EU Peer Review, the conclusions of which were published by FFSA in April 2006 [EFSA Scientific Report (2006) 67, 1-61]. Eventually ethephon was included in the Annex I of Directive 91/414 on 1 August 2007. The toxicity endpoints were up-dated in September 2008 [EFSA Scientific Report (2008) 174, 1-65] while the residue definition for dietary risk assessment was modified in the context of the review of the existing EU MRLs according to article 12 of Regulation 396/2005 [EFSA Journal 2009; 7(10):1347].

Extensive residue and metabolism data for ethephon were sponnitted to EU authorities and EU Member States in the context of the EU Dossier for the Aprex I inclusion of the active substance under Directive 91/414/EEC (Baseline Dossier). The present Supplemental Dossier for the renewal of the approval of ethephon only include studies which were not art of the Baseline Dossier, either because they are new and were not available at the time when the Baseline Dossier was issued, or because they were not relevant to the user supported in the Baseline Dossier. The studies of the Baseline Dossier, which were already valuated during the previous EU review, are not summarised again in detail, but if these studies are still considered relevant the mater conclusions from the previous evaluations are provided. The representative use for the renewal of the approval of ethephon is the same as the representative use for the inclusion in Annex for Directive 91/414, namely prevention of lodging and shortening of stems in wheat and barley. However, the Supplemental Dossier also includes some storage stability and metabolism data that are not directly relevant to the representative use but are necessary to support other uses of the active substance and should preferably be evaluated in the context of the upcoming Euleview.

CA 6.1 Stocage stability & residues

Table 6.1- 1 provides an overview of the storage stability data included in the Annex II dossier of 2002 and reviewed by the Rapporteur Member State in the Draft Assessment Report (DAR) of April 2004. In the following, detailed summaries are provided for supplementary storage stability studies that were not included in the Annex II dossier of 2002 and, therefore, not reviewed in the DAR.

Table 6.1-1 Overview of the storage stability data for ethephon and its metabolite HEPA in plant matrices submitted in the Annex II dossier of 2002 and evaluated in the DAR of 2004

Document	Matrix	Category [rich in]	Analyte	Storage conditions	Stability odemonstrated for up to
M-187521-01-1 (R013222)	Wheat grain	Starch	Ethephon	frozen at ca20°C	244months
M-187519-01-1 (R013221)	Wheat straw	-	Ethephon	frozen@ca26%C	24 months
M-187533-01-1 (R013228)	Tomato fruit	Water	Ethephon	if Gen at & -20°C O reeze-ded at room temperture	24 months
M-187515-01-1 (R013219)	Apple fruit	Water	Ethephon Q	frozen at ca. The C frozen at ca. The C frozen at ca. The C	24 nonths 24 Conths
M-187544-01-1 (R013233)	Grape berry	Acid	Ether on	Oozen a Ca20 C freeze Lied at room temberature	months 24 months
M-187511-01-1 (R013217)	Blackberry fruit	Acid	Ethephon (frozen at ca 20°C freeze-dried at roomtemperorire	24 months 24 months
M-187525-01-1 (R013224)	Cottonseed	Oil O	Ethephon (frozena ca200	24 months
M-188009-01-1 (R013470)	Apple juice Cottonseed oil	- 8	Ethepla ,	fræen at cæ220°C frozen as ca2036	12 months 12 months
M-210332-01-1 (C020900)	Wheat grain	Starch Valer	EPA C	frozen at ca. 18°C fro@n at ca 18°C	3 months 3 months

Report: KCA 6.1/11 1992; NF187505-01-1

Title: Storage subility Stody of Ethephon in/on whole Fresh Cherries

Document No. M-187905-01

Guideline(s): USEPA (=EPA): 17 PAE

Guideline deviation(s):

GLP/GEP:

Materials and methods

Untreated ground cherry samples (200) were fortified with ethephon at a concentration of 1.0 mg/kg and then either stored froze at -15 °C or freeze-dried and stored at room temperature. Ripe sweet cherries (variety temperor) were used for this study to avoid the stabilising effects of the greater acid content of sour cherries. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored ortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether



and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD).

Findings

As shown in Table 6.1-2, the procedural recoveries for ethephon were satisfactory at all storage intervals. The recoveries from the stored fortified samples were also satisfactory and did not evidence any degradation.

Conclusion

The residues of parent ethephon in cherry samples were shown to be stable for at least 24 months following storage at -15°C. The residues of ethephon in cherry samples were also stable for at least 24 months following storage at room temperature after freeze drying.

Table 6.1-2 Storage stability of ethephonic cherry

		-	•		**		
Sample material	Compound	Storage conditions	Storage period	Recoveries from	stored %)	Procedural rec from freshly f samples (ortified
		()) period?	Individan values	Werage,	♥ Individual ✓ values	Average
			Day 0 🍫	9 30, 95 Q	93	84	-
			1 month	° 12, 1,160	· 11	116	-
			2 months	91 ×	98	112	-
Charmy	Ethonbor	frozen at	6 months	93, 70	92	103	-
Cherry	Ethephon	ca. _{\sigma} -15°C _{\sigma}	9 months	93, 70	82	77	-
	, Ø %		125 months	86, 85	86	99	-
			18 months	97, 80	89	104	-
·			24 months	102, 90	96	98	-
			Day 0	91, 95	93	84	-
8		\(\display\)	1 mortin	111, 97	104	108	-
(2 months	105, 95	100	80	-
Chevry	E thephor	freeze-dried	Omonths	94, 110	102	105	-
Chexgry	Extreprioria	temperature	9 months	104, 89	97	104	-
		0	12 months	89, 89	89	82	-
	T A	~ ~	18 months	81, 70	76	96	-
			24 months	83, 85	84	101	-



Report: KCA 6.1/12; 1991; M-187529-01-1 Storage stability of ethephon in/on walnut nutmeats

Report No.: R013226 Document No.: M-187529-01-1

Guideline(s): USEPA (=EPA): 171-4(E)

Guideline deviation(s): not specified

GLP/GEP: yes

Materials and methods

Untreated samples of ground walnut meat (20 g) were fortified with the phon at a concentration of 0.2 mg/kg and then either stored frozen at \leq -15°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted or day 0 and after 1, 3, 5 and 6 months of storage (depending on the type of storage). At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed. On Day 0 and at the 5 month interval, the analysis was repeated with one or two additional sets of samples.

The samples were analysed for ethephon using the method SOP 90069. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The do samples were soxhlet extracted with methanol. Thereafter, the extract was acid fied by addition of 10% HCl in methanol and frozen overnight at -10°C to solidify lipid materials. The remaining methanolic extract was concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The emphon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD):

Findings

As shown in Table 3, the study results were quite inconsistent since the first series analysed on day 0 showed an average recovery rate of only 36% while better recoveries were obtained from samples stored for up to months. The variability of the results may be attributed to the lack of repeatability of the residue analytical method and the low recoveries from some of the stored samples do not necessarily indicate that the residues degraded during storage.

Conclusion

The study is considered to be inconclusive.

Table 6.1-3 Storage stability of ethephon in meat of walnut

Sample material	- I Compolina I -				Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
materiai	·	conditions	period	Individual values	Average	Individual vagres	Average	
			Day 0	31, 40	3@	, ©112 A	<u> 1</u> 12	
			Day 0*	107, 84, 126, 87	101	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∜71	
Meat of walnut	Ethephon	frozen at ≤ -15°C	1 months	846.93) 89 ₆		81 。	
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			3 months	108, 105	1000	64 6	Ã	
			5 months	69, 74, 66, 83	<u></u> \$ [©] 73	® 87, 89	88	
			Day 0	3640	7 36 C	P12 @	112	
		freeze-dried	Day 💞	107,84,126,87	\$400,1	72, 76	71	
Meat of walnut	Ethephon	at room	1 months	91,	∠ 83 _ (88	88	
		temperature	5 months	64, 50, 42, 77	59	6 7, 79	73	
		Č	6 months	\$73, 83\$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	73	73	

^{*} Second set

Report: KCA 5.1/13; 1992; M-16\s41-01-3

Title: Descrimination of the Storage Stability of Etherston in Pineapple Forage

Report No.: **R91**3230@

Document No.: M-161844-01-

Guideline(s): USEPA (=EPA). 171-4

Guideline deviation(s) -- -

GLP/GEP:

Materials and methods

Untreated ground samples of pineapple orage (20 g) were fortified with ethephon at a concentration of 0.5 mg/kg and there ither stored frozen at about -20°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day and after 1, 2,4, 6, 9,42, 18 and 24 months of storage. At each interval, two stored fortified samples one stored control sample and one freshly fortified sample were analysed. In two cases, the stored samples of elded ow recoveries and the results were checked by analysing a second set of samples.

The samples were analysed for Thephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. The eafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with flame photometric detection (GC/FPD). Since the method had not been used to analyse pineapple forage previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1-4, the method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals (Table 6.1-6). No degradation was observed in the samples stored at about -20°C, as evidenced by satisfactory recoveries at all storage intervals up to 24 months. The residues in the freeze-dried samples stored at ambient temperature seemed to be less stable since low recoveries were obtained at the 12 month and 24 month storage intervals (55% and 57%, respectively).

Conclusion

The residues of parent ethephon in pineapple forage samples were shown to be stable for at least 24 months following storage at about -20°C. However, the residues of ethephon in pineapple forage samples were shown to be stable for only 9 months following storage at room temperature after freezedrying.

Table 6.1-4 Validation of the method SOV 90070 for the determination of ethermon in pineapple forage

Report (Method)	Matrix	Forthfication level () [mg/kg/]	.s.	Individual recoveries	Mean recovery [%]	RSD [%]
M-161841-01-1 (SOP 90070)	Pineapple forage	0.20 0.50 overall		77, 82, 89, 92, 101, 118 88, 89, 90, 95, 95, 96 77, 87, 87, 92, 92, 94	77 82 85 81	7.7 3.2 5.2 6.7

Table 6.1-5 Storage stability of ethephon in pineapple for age

Sample «		d storage Storage conditions period		Regoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
material			period (Average	Individual values	Average
*			Dag	82, 79	81	76	-
4			1/month	95, 85	90	79	-
			2 months	90, 86	88	90	-
<			4 months	106, 82	94	100	-
Pineapple forage	Ethephon	frozen at ca28°C	6 months	81, 72	76	92	-
		10	9 months	85, 88	87	85	-
	Õ		12 months	82, 89	85	89	-
			18 months	84, 95	89	93	-
			24 months	86, 98	92	83	-



Sample	Sample material Compound		Storage period	Recoveries from samples (Procedural rec from freshly fo samples (ortified
materiai		conditions	periou	Individual values	Average	Individual	Average
			Day 0	82, 79	81	76	5 - B
			1 month	73, 86	79	74	
			2 months	92, 99°°°°	98	850	% -
		freeze-dried	4 months	92,20	5 91 <u>(</u>		> -
Pineapple forage	Ethephon	at room	6 months	S , 88 ,	88	× 85 × 85	
		temperature	9 months	076,74	₄ @75	, W 900 ,	Ŵ -
			12 months	Q49, 70, 51, 53 %	55 °	80°85 Q	83
			18 months	3 7,77 &	70	96	-
			24 momhs	52, 59, 50, 63	£ , 57	89, 💇	86

^{*} The recoveries shown in this table were not corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-palculated based on the corrected values and the procedural recoveries.

Report: KCA 6.1/1/4; 1992; M-3/87540-91-1

Title: Determination of the Storage Stability of Ethephor on Pineapple Fruit

Report No.: R013231

Document No.: M\$87540.01-1

Guideline(s): DEPA (EPA): 171-46

Guideline deviation(s): C-GLP/GEP: ves

Materials and methods

Untreated ground samples of pineapple fruit (20 g) were fortified with ethephon at a concentration of 0.5 mg/kg and then either stored frozen at about ©0°C or freeze-dried and stored at room temperature. In order to monitor an operation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 4, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored fortified samples, one stored control ample and one treshly fortified sample were analysed.

The samples were analysed for ethephor using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diagomethane. The ethephon dimethyl ester was analysed by gas chromatography with flame photometric detection (GC/FPD). Since the method had not been used to analyse pineapple fruit previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1-6, the method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals (Table 6.1-7). The recoveries from the stored fortified samples were equally satisfactory at all storage intervals and for both types of storage conditions. Therefore, no degradation was observed.

Conclusion

The residues of parent ethephon in pineapple fruit samples were shown to be rable for at least 24 months following storage at -20°C. The residues of ethephon in pineapple fruit samples were also stable for at least 24 months following storage at room temperature after freeze-drying.

Table 6.1-6 Validation of the method SOP 90070 for the determination of ethephon in pineapple fruit

Report (Method)	Matrix	Fortification level/ [mg/kg]	Number of replicates	Individual recoveries	Mean recovery [%]	RSD [%]
M-187540-01-1 (SOP 90070)	Pineapple fruit	0.05 0.20 0.50 0.50	6 8 8 18	79, 82, 80, 92, 104, 118 88, 89, 90, 95, 95, 96 77, 87, 87, 92, 92, 94	93 92 88 91	15.8 3.8 7.0 10.0

Table 6.1-7 Storage Cability of ether from in pineapple fruit

			* \$`				
Sample	Compound	napound Storage		Recoveries from	m stored %)*	Procedural recoveries from freshly fortified samples (%)	
material		conditions	period 2	In @ ividual Svalues	Average	Individual values	Average
		& 1	Day 0 €	86, 86	86	83	-
			month O	88, 93	91	79	-
<i>G</i> (1			2 months	95, 95	95	93	-
4		\bigcirc	4 months	96, 117	106	94	-
Pineapole frug	Ethephon	frozen at	months	108, 106	107	98	-
*			9 months	90, 90	90	102	-
			12 months	87, 79	83	99	-
		, O	18 months	117, 112	114	110	-
	Ť		24 months	77, 98	88	86	-



Sample	- I (omnound I		Storage	Recoveries from samples (%		Procedural rec from freshly fo samples (ortified
material		conditions	period	Individual values	Average	Individual	Average
			Day 0	86, 86	86		5 - B
			1 month	89, 86	88	73	
			2 months	100, 93°	96	890	\[\]
		freeze-dried	4 months	90,29	\$ 95 K		> -
Pineapple fruit	Ethephon	at room	6 months	9 2 , 102	97	×82 ×	* °
		temperature	9 months	©103, 9£°	_{&} @97	(C) 89(C)	Ŵ -
			12 months 4	Q 98,94 %	96)) -
			18 months	19 6, 86	<i>2</i> 6	7102	-
			24 morths	75, 8 Q	. 79 L. 79	870	-

^{*} The recoveries shown in this table were not corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-calculated based on the corrected while and the procedural recoveries.

Report: KCA 6.1/1/5; 1992, M-187542-01-

Title: Storage/Stability Study of Ethephon in/one whole fresh Peppers

Report No.: R01\$232

Document No.: M\$87542\$\text{\$\text{\$\cdot\$}}-1

Guideline(s): SEPA (=EPA): 171-4E

Guideline deviation(s):

Materials and methods

Untreated ground samples of green bell perper (20 g) were fortified with ethephon at a concentration of 1.0 mg/kg and then either stored frozen at -15°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 2, 4,6,9, 12,18 and a months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070, which was slightly adapted. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxillet extracted with 05% tartaric acid in methanol. Thereafter, the extract was acidified by addition of 10% HCL in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD).

Findings

As shown in Table 6.1-8, the procedural recoveries for ethephon were usually in the guideline range of 70-110% but frequently exceeded the upper limit of 110% with a maximum of 130% (which was



found at several storage intervals). However, the recoveries from the fortified samples stored at -15°C also exceeded the upper limit of 110% frequently and actually were very comparable to the procedural recoveries. It may be concluded that parent ethephon remained stable in green bell pepper upon storage at about -15°C for at least 24 months. Quite different results were obtained for the fortified samples of green bell pepper which were first freeze dried before storage at room temperature. For these samples satisfactory recoveries (similar to the procedural recoveries) were obtained at the three first storage intervals (day 0, 2 months, 4 months) while at the next intervals the recoveries were found to decrease progressively down to about 37% at the 24 month storage interval.

Conclusion

The residues of parent ethephon in pepper samples were shown to be stable for at least 24 months following storage at -15°C. However, these residues were found to be stable for only 4 months following storage at room temperature after freeze-drying.

Table 6.1-8 Storage stability of ethephon in green sell pepper

					, (O)	(O' 2\	
Sample material	Compound	Storage conditions	Storage Deriod	Recoveres from	n stored	Procedural rec from freshly for samples (ortified
material		Č		Individual values	Average	Individual values	Average
			Day 0	→ 120, ¥10 (115%	130	-
			months	12 0, 110	105	110	-
Bell pepper			4 months	100, 100	700	98	-
	Ethonbon	frozen	6 months	100,87	94	110	-
	Ethephon	ca18°C	√9 months	Ø2, 78€	85	100	-
		\$ 4	12 ponths	\$ 88, 9 6	92	85	-
			18 months	1,10, 120	115	110	-
4			24 months	2 20, 130	125	130	-
		W _W	Pay 0 &	120, 110	115	130	-
			months	110, 100	105	130	-
8		Y É	4 months	92, 93	93	82	-
Bell pemper	Ethephon	freeze-d@ed at room	months	62, 83 97*, 85*	73 91*	120 110*	-
		temperature	9 months	47, 57 70*, 60*	52 65*	96 98*	-
		0	12 months	42, 46	44	87	-
			18 months	37, 36	37	130	-

^{*} Result obtained during re-analysis.

Note: In the report, the results are provided in mg/kg. However, the recovery rates can be calculated easily based on the fortification level of $1.0 \, mg/kg$



Report: KCA 6.1/16; ; 1993; M-187507-01-1

Title: Determination of the Storage Stability of Ethephon in Cantaloupe Fruit

Report No.: R013215
Document No.: M-187507-01-1

Guideline(s): USEPA (=EPA): 171-4e

Guideline deviation(s): -- yes

Materials and methods

Untreated ground melon samples (20 g) were fortified with ethephon at a concentration of \$5 mg/kg and then either stored frozen at about -20°C or freeze-drief and stored at from temperature. In order to monitor any potential degradation of ethephon upon storage analyses were conducted on day and after 1, 2, 4, 6, 9, 12, 18, 24, 30 and 36 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Sox det extracted with methanol. Thereafter, the extract was acidified by addition of 10% HC in methanol and concentrated under a stream of nitrogen. Solid materials were provipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The thephon dimethyl estern as analysed by gas chromatography with flame photometric detection (GC/FPE). Since the method had not been used to analyse melon fruit previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1- The method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactors at all storage intervals (Table 6.1- 10). The recoveries from the fortified samples stored at about 20°C were equally satisfactory at all storage intervals. Therefore, no degradation was observed up to 36 months of storage. Quite different results were obtained for the fortified samples of melon which were first freeze dried before storage at room temperature. For those samples satisfactory recoveries (similar to the procedural recoveries) were obtained at the first four storage intervals (day 0, 1 month, 2 months, 4 months) while at the next intervals the recoveries were found to decrease progressively down to 12% at the 18 month storage interval.

Conclusion

The residues of parent thephoto in melon samples were shown to be stable for at least 36 months following storage at about 20°C. However, these residues were found to be stable for only 4 months following storage at room temperature after freeze-drying.



Table 6.1-9 Validation of the method SOP 90070 for the determination of ethephon in melon

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-187507-01-1 (SOP 90070)	Melon fruit	0.05 0.20 0.50 overall	6 6 6 18	74, 74, 67, 76, 77, 71 71, 80, 82, 81, 70, 84 79, 78, 76, 65, 74, 80	· 73 78 73 73	5.0 7.6 503 40.4

Table 6.1-10 Storage stability of ethephon in melon

Sample material Compound Storage conditions Storage period Period Samples (%) Storage period Procedural recover from freshly Stiric Samples (%) Samples (%) Average Values	ries fied verage
Average Individual Average value Average	verage - -
1	<u>-</u>
	_
79,90 5 76	
2 months 4 96 80 591 83	-
4 Chonths 97,97 97 105	-
% 06 months 407,99 99 99	-
Melon Ethephon Ca20°0 9 months 103,92 3 97 90	-
Meion Ethephon Ga20°0 9 Hondris 103,92 97 90 12 months 84,84 84 93	-
18 months 75 ,80 78 80	-
24 wonths 82 32 82 77	-
36 months 103,111 112 105	-
36 mearths 98,98 98 104	-
12 months	-
© © month 80,76 78 83	-
2 months /6,64 /0 /3	-
Melon Ethephon at room Amonths 102,95 99 88	-
temperature 6 months 59,37 48 89	-
6 months** 47 ,38 42 106	-
18 months 12 ,12 12 81	-

^{*} The recoveries shown in this table were <u>not</u> corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-calculated based on the corrected values and the procedural recoveries.

^{**} A second set of samples was analysed at this storage interval.



Report: KCA 6.1/17; ; 2015; M-537340-01-1

Title: Short-term storage stability of ethephon in/on cereals (grain) and the processed

fractions (wholemeal bread, starch, malt sprouts and beer)

Report No.: MR-15/138
Document No.: M-537340-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21

October 2009 concerning the placing of plant protection products on the market OECD Guidelines for the Testing of Chemicals. Stability of Pesticide Residues in

Stored Commodities. 506. 2007-10-16.

US EPA OCSPP 860.1380, Storage Stability, Data

Guideline deviation(s): none GLP/GEP: yes

During the barley and wheat processing studies 14-3400 and 14-3401 the examination samples intended for the analysis of parent ethephon residues were stored in a freezer room at a nominal temperature \leq -18°C. However, for 15 hours and 18 minutes the actual temperature in this freezer room exceeded the tolerance of -18°C, with an average of -6.0°C, during this time the temperature was higher than -10°C for about 12 hours and 35 minutes with an average of -4.6°C. The maximum temperature was -1.2°C. The purpose of the study P642151808 was to investigate the impact of this temperature deviation.

Materials and methods

Control samples (5 g) of cereal grain and eereal processed commodities (wholemeal bread, starch, malt sprouts and beer) were fortified with ethephon at the 10-fold LOQ level of 0.10 mg/kg and first stored in a freezer at \leq -18°C. After a few days the samples were taken out of the freezer and stored in a refrigerator for 24 hours. The temperature in the refrigerator range between -0.5°C and 5.9°C for the samples of grain, whotemeal bread, starch and malt sprouts, and between 0°C and 5.7°C for the samples of beer. Afterwards the samples were stored again at \leq 48°C in a freezer until analysis. For each sample material and storage interval (immediate malysis on day 0 or analysis after storage) the analytical series consisted of one control sample, two freshly fortified sample for procedural recovery determination and three stored for the samples.

The residues of ethephon in/or cereal Ograin and the processed fractions (wholemeal bread, starch, malt sprouts and been were determined according to the method 01429. For beer the residues were extracted once with methodol. For cereal grain and all other processing materials the residues were extracted by blending three times with prothanol followed by digestion with a mixture of hydrochloric acid (32%) /water (127, v/v) at 50°C overnight. After addition of isotopically labelled internal standard the extracts were analysed by HPL MS/MS. The procedure was validated for cereal grain as part of the initial validation. Further validation for the wheat and barley processed commodities was performed during the processing studies 3-3406 and 14-3400, respectively. The limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain and the cereal processing fractions (including been).

Findings

As shown in Table 1-11, the procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals. The average recoveries from the fortified samples stored for 24 h at between -0.5°C and 5.9°C and about one month at \leq -18°C ranged between 91% and 104%. These values were very comparable to the average recoveries determined on the day of fortification. Therefore, the residues of ethephon in cereal grain, wholemeal bread, starch, malt sprouts and beer remained stable upon storage for 24 h between -0.5°C and 5.9°C.

Conclusion

The residues of ethephon in cereal grain, wholemeal bread, starch, malt sprouts and beer were shown to be stable for at least 24 h under refrigerated storage between -0.5°C and 5.9°C.

Table 6.1-11 Storage stability of ethephon in cereal grain and cereal processed-commodities

				♠		de la company
Sample material	Compound	Storage period and conditions	Recoveries from samples (%) Individual values		Procedural rec from freshly fo samples (Indiordual values	ortified
		Day 0	8, 93, 90	94 @	(100, 2)	6 97
Barley grain	Ethephon	28 days frozen & 1 day refrigerated	Q100, 102, 104 %	102	100, 99	103
Wheat		Day 0	98 , 98, 9 5	% 6	96, 940)	95
wholemeal bread	Ethephon	28 days frozen & 1 day refrigerated	\$ 88, 8 \$ 94	\$\frac{1}{2} 90 \times	9 9 , 92	96
Barley malt		Day 8	100, 90, 91	, 9 9	96, 95	96
sprouts	Ethephon	31 days frozen &	% 96, 9 © 96	95	102, 106	104
Wheat		Day	100 , 90, 85		76, 100	88
starch	Ethephon	31 days frozen & 1 day efrigerated	89, 94, 94	92	91, 90	91
	Ď	S Day 0	105 901, 102	102	100, 104	102
Barley beer	Ethephon	23 days frozen & 1 days efrigerated	98, 102, 96	99	98, 105	102

^{*} For the samples that were not analysed on day 0, storage was performed at ≤ -18°C, except for 24 h during which the samples were stored refrigerated between -0.5°C and 5.9°C (except for beer : between 0°C and 5.7°C).

Report: KCA 6.1/18; 2003; M-234800-01-1

Title: Storage stability of AF 1020271 in wheat grain and tomatoes

Report No: C034370

Document No.: **W**-234800-01-1

Guideline deviation(s):
GLP/GEP:

In many residue studies the samples were analysed for the metabolite HEPA in addition to parent ethephon. The storage stability of HEPA was investigated in wheat grain and tomato fruit. At the time when the previous dossier was submitted results were only available for storage periods up to 3 months (refer to the document M-210332-01-1 in Table 6.1-1). However, the study was continued for up to 18 months of storage and the final results are reported in the document M-234800-01-1. It is important to note that, due to its favourable toxicological profile, HEPA is not part of the existing and



proposed residue definitions for dietary risk assessment or MRL setting. Therefore, no storage stability data on HEPA are needed to demonstrate consumer safety.

Materials and methods

Untreated ground samples of wheat grain and tomatoes (10 g) were fortified with HEPA at a concentration of 0.5 mg/kg and then stored frozen at less than -18°C. In order to monitor any potential degradation of HEPA upon storage, analyses were conducted on day 0 and after 143, 6, 12 and 18 months of storage. At each interval (except on day 0), two stored fortified samples, order stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP HVA 10077. The residues were extracted from the samples with methanol. After liquid fiquid partitioning with methyl effer, the residues were methylated with diazomethane. The HEVA derivative was analysed by gas chromatography with flame photometric detection (SC/FPD).

Findings

As shown in Table 6.1-12, the procedural recoveries for HEPA were in the mideline range of 70-110%. The average recoveries from stored for fined samples ranged between 73% and 102% in wheat grain and between 83% and 108% in tomato fruit. The somewhat low recoveries of 73% and 74% determined in wheat grain at the month and 12 month storage intervals were not confirmed at the last storage interval of 18 months (recovery of 102%). It may be concluded that the residues of HEPA are stable for at least 18 months in wheat grain and tomato fruit samples stored at or below -18°C.

Conclusion

The residues of HEPA in samples of wheat grain and torgato fruit were shown to be stable for at least 18 months at or below -18°C.

Table 6.1- 12 Storage stability of HERA in wheat grain and tomato fruit

Sample	Storage	Storage &	Recoveries from samples (Procedural rec from freshly f samples (ortified	
material Compound Conc	conditions	period O	Individual values	Average	Individual values	Average	
4		Day 0	93, 83	88	-	-	
		Frozen at S	I month	95, 95	95	85	-
4			3 months	88, 92	90	97	-
wheat grain	Wheat grain Etherhon	ງັ≤-18°ີC	6 months	66, 80	73	103	-
	- "O" -	12 months	78, 69	74	81	-	
			18 months	98, 106	102	102	-



Sample material	Compound	Storage conditions	Storage	Recoveries from samples (Procedural rec from freshly fo samples (ortified
materiai		conditions	period	Individual values	Average	Individual	Average
			Day 0	85, 85	85 ू		\$ - B
			1 month	111, 95	111,95 103		
Tomato fruit	Ethanhan	frozen at	frozen at 3 months 92, 105°	99	970	\$\frac{3}{2}-	
Tomato muit	Ethephon	≤ -18°C	6 months	80,85	S 83 . L		> -
			12 months	8 , 97	′ 89 ₀	₹88 Å	Ø -
			18 months	(10, 10g)	å08	(W) 102C	Ŵ -

Table 6.1- 13 provides an overview of the previously submitted storage stability data and herein provided supplementary storage stability data. The storage stability study in nutment, which was not conclusive, is not listed. Overall, the storage stability of thephoa was established for at least 24 months in deep frozen samples of 5 matrices with a high water content, 3 matrices with a high acid content, 1 matrix with a high starch content and one matrix with a high oil content.

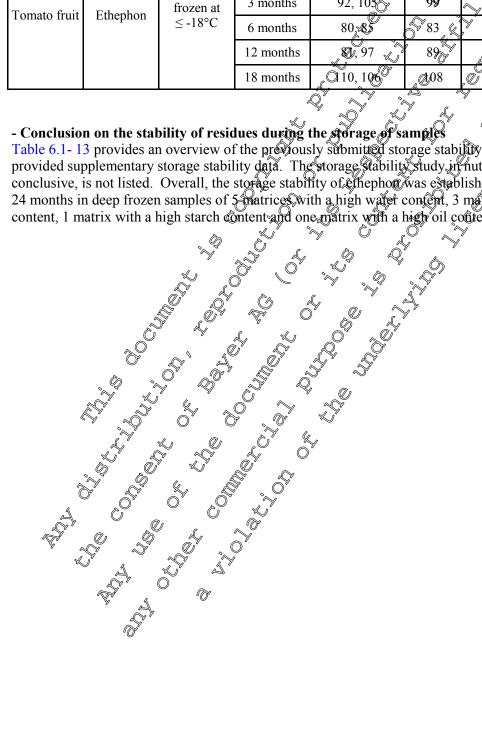


Table 6.1-13 Overview of the storage stability data for ethephon and its metabolite HEPA in plant matrices (compilation of previously submitted and supplementary data)

Document	Matrix	Category [rich in]	Analyte	Storage conditions	Stability demonstrated o for up to
M-187521-01-1 (R013222)	Wheat grain	Starch	Ethephon	frozen at ca20°C	24 mQths
M-187519-01-1 (R013221)	Wheat straw	-	Ethephon	frozen doså20°C/	54 months
M-187533-01-1 (R013228)	Tomato fruit	Water	Ethephon	frown at ca 20°C 4 from the care of the ca	24 conths 24 months
M-187515-01-1 (R013219)	Apple fruit	Water	Ethephon	Prozen &ca21	24 mores 24 morths
M-187505-01-1	Cherry	Water	Ethephon	frozen at ca -15°C of the control of	24 months 0 months
M-187542-01-1	Bell pepper	Water	Ethephon (frozetrat ca\$5°C	24 months 4 months
M-187507-01-1	Melon	Water	Etherson	frozen at ca20% Conference at case of the frozen at the conference at the confere	36 months 4 months
M-187544-01-1 (R013233)	Grape berry	AĞd Ç	thephon	frozen at ca 270°C fr@ze-dric@at room temperature	24 months 24 months
M-187511-01-1 (R013217)	Blackberry fruit	Acid	Etherhon 7	Prozen LQca20% freeze-dried aN foom temperature	24 months 24 months
M-187540-01-1	Pineapple Fruit	Reid	Ethephon	frozen at ca -20°C Geeze-drod at room temperature	24 months 24 months
M-161841-01-1	Pincapple farage	- 1	Eta phon	frozerCat ca20°C free2e-dried at room temperature	24 months 9 months
M-187525-01-1 (R013224)		Oil O	Ethephon	Gzen at ca20°C	24 months
M-188009-01-1 (R013470)	Apple juice Esttonse o oil		Ethephok,	frozen at ca20°C frozen at ca20°C	12 months 12 months
M-234800-0174	Wheat grain Tornato fruit	Starck Water	HEPA	frozen at ca18°C frozen at ca18°C	18 months 18 months

CA 6.2 Metabolism, distribution and expression of residues

The Annex II dossier of ethephon submitted in 2002 includes two GLP metabolism studies for foliar application of ethephon in wheat and tomato, respectively. In all studies the main degradation route of ethephon was shown to involve decomposition to ethylene and phosphates. Ethylene is rapidly released into the atmosphere while the phosphates are taken up in the natural phosphate cycle of the plant. However, part of the applied ethephon is metabolized according to a different metabolic pathway that results in the formation of the metabolite (2-hydroxyethyl)phosphonic acid (abbreviated HEPA). HEPA is further metabolized by incorporation of the two carbon atoms in natural biomolecules. In the wheat study ¹⁴C-ethephon was foliar sprayed at the rate of 360 g as/ha when the



plants had reached the ligule stage (BBCH 39). At mature harvest, grain showed similar levels of parent ethephon and HEPA (0.47 mg/kg and 0.51 mg/kg, representing 43.5% and 47.7% of TRR, respectively) whereas straw was found to contain higher levels of ethephon than of HEPA (1.47 mg/kg and 0.62 mg/kg, representing 62.3% and 26.1% of TRR, respectively). In the tomato study the plants were foliar-treated with 1440 g a.s/ha of ¹⁴C-ethephon. Parent ethephon was found to be the major residue component in tomato fruit harvested 0, 5 and 12 days after treatment (\$6.1\% of TRR on day 0) and 47.1% of TRR on day 12). HEPA represented up to 15% of the total radioactive residue.

The Annex II dossier also includes non-GLP studies and publications on the metabolism of etheration in pineapple, summer squash, cucumber, apple, cherries and gape. Despite many limitations these non-GLP data were consistent with the results of the two GLP studies since hydrolysis of ethephon to ethylene was shown to be the main metabolic pathway and HEPA was sometimes identified as a minor residue component. They also provided information on the formation and incorporation of phosphates.

Besides the wheat and tomato metabolism studies a GLP cotton metabolism study is also available. This study is reviewed below since it was still on-going at the time when the Anne II dossier of ethephon was issued.

Report: KCA 6.2.1/08;

Title: Metabolism of [Lol4C]-Ethephon in cotton

Report No.: B003904 Document No.: M-240888-01

M-240888-01-2 USEPA (=EPA): 860/1300 and EU 91/4/14/EEE not specified yes Guideline(s):

Guideline deviation(s):

GLP/GEP:

Materials and methods

Cotton plants growing in an outdoor (bot (1,28 m²) were folial treated with 14C-ethephon (specific activity 36 µCi/mg). The application rate was 1406 g as/ha which approximately corresponds to the maximum application rate of 1440 g as/ha for the use of ethephon in cotton in the field. Samples for analysis were taken at day 0 just after treatment (foliage), and 7 days after treatment at harvest maturity (gin trash and bolls). The bolls were separated into lint (which was not analyzed further) and seed.

The day 0 folioge samples were first wished with acetonitrile to recover surface residues. The washed foliage was then extracted with aceta witrile. The final harvest (mature) samples were frozen and ground prior to being analyzed further. Sample aliquots were combusted to determine the total radioactive residues. Thereafter, the gingrash samples (principally leaves and boll husks) were extracted with methanol. Fibers were separated from the extracts by filtration. In order to remove oil, the seed extracts were repeatedly partitioned with hexane prior to analysis. The radioactivity in washes and extracts was measured by LSC. The radioactivity remaining in the fiber was determined by combustion. Extracted fibers from the gin trash and seed were hydrolyzed with a mixture of concentrated hydrochloric acid and water (1/7, v/v). The samples were incubated for 20 hours at room temperature, then filtered and washed with methanol. The radioactivity extracted in the acid hydrolysate (filtrate plus methanol wash) was measured by LSC. The residual fiber was dried and the radioactivity remaining unextracted quantified by combustion.



The individual radioactive residues in the extracts were identified and quantified by high performance liquid chromatography (HPLC) against a mixture of analytical reference standards. Identification was confirmed by thin layer chromatography (TLC).

Findings

The total residues in foliage at day 0 averaged 237.3 mg/kg ethephon equivalents (average of two samples) while 7 day later analysis at final harvest showed 31.4 mg/kg ethephon equivalents in the crim trash and 0.8 mg/kg ethephon equivalents in the cotton seed. The residue levels and extraction profiles at each time point are presented in Table 6.2.1-1.

There was significant variability between the two samples at day 0 as might be expected given the small sample size at this time point. The total residue (a determined by extraction and combustion) in the day 0 samples ranged from 113.7 mg/kg to 360.8 mg/kg etherhon equivalents. The recovery of the residue at Day 0 by acetonitrile wash and extraction was relatively inefficient, but this was used only to establish the residue levels at day 0 and to develop extraction methodology for the smal harvest.

At final harvest, the residue levels and extraction profiles for the replicate samples were comparable. Methanol extraction of mature gin trash and seed proved very effective recovering over 80% of the total radioactive residue. Acid hydrolysis recovered the majority of the remainder of the residue (11-17% TRR), leaving only 0.2% TRP fiber bound in the gir trash and 1.2% bound in the cotton seed.

Table 6.2.1-1 Total Radioactive Residues (TRR) and extractability of residues in cotton samples

Sample	Sample	TRRQ	Surface	Wash	Matrix 1	Extract	Ac hydrol		Non extr	
type		PP 01	Ç% TRR≪	J ppm	ॐ TRR	Žppm	% TRR	ppm	% TRR	ppm
	Ď	\$13.7 4	50 %	57.6	1.5	1.7	na	na	48.3	54.9
Day 0 Leaves	Ç 2P ∑	3603	3 .0	263.3	0.3	1.0	na	na	26.8	96.6
	Mean	23 7.3	61.6	∦160.1 [≈]	0.9	1.4	na	na	37.6	75.8
	,3 3 5	30.0	nã	p a	89.5	26.8	10.4	3.1	0.1	0.04
Day 7 Gin Trash	√ 4P √	328	na	Q _n a	87.7	28.8	12.0	3.9	0.3	0.11
	Mean	31.4	na 🖔	na	88.6	27.8	11.2	3.5	0.2	0.08
21	PA A	0′0.82	na	na	84.1	0.69	14.9	0.12	1.0	0.008
Day 🕽 🗡	7PB	* 🤍	na	na	80.0	0.66	18.6	0.15	1.4	0.011
S	Mean	0.82	na	na	82.1	0.67	16.8	0.14	1.2	0.010

Notes

- ppm = mg equivalents of ethepson per kg of sample.
- na = not applicable
- The total radioactive residue (TRR) in the day 0 samples was calculated by summation of the radioactive residues determined in the various fractions (wash, extract and fiber). The TRR at Day 7 was determined by combustion.

Chromatography of the day 0 surface washes confirmed that they were primarily composed of parent ethephon (mean of 59.2% TRR). A further 0.2% of the radioactivity was identified as



(2-hydroxyethyl)phosphonic acid (HEPA), with no other single metabolite representing more than 1.5% TRR. The remainder of the radioactivity was not extracted from the fiber.

Chromatography results of the individual extracts at final harvest showed excellent correlation. The majority of the residue in the gin trash and cotton seed (93.0 and 78.3%, respectively) consisted of unchanged parent. The only significant metabolite was HEPA representing 1.7% TRR in the gin trash and 9.6% TRR in the cotton seed. A total of 88-95% of the residue in these CACs was identified as ethephon and HEPA, with no other single metabolite comprising more than 1.9% of the residue. The mean results are shown in Table 6.2.1-2. Identification by HPLC was confirmed by TLC.

Table 6.2.1-2 Identification of ethephon residues in cotton samples

Sample type	Extract Type	Total Extractable Residue		Ethe	Ethephon		P STEPA O		Single nown	Total Mentinec	
		% TRR	ppm	% TRR	ppm §	Ø TRR	p pm	%/TRR	ppm	%FRR	ppm
Day 0 Leaves	Acetonitrile wash	61.6	160.1	\$90 590 500	156.3	0.25	0.2	0.9	2.10	59.4	156.5
Day 7	Methanol/Water extract	88.6	27.8	\$83.7 ************************************	ł	\$\) 1.3	©0.4	∑¶1.3 2 1.3	0.4	85.0	27.1
Gin Trash	Acid hydrolysate	11.2	3.5 Ø	\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	~Z,9	0.A			0.3	9.7	3.1
	Combined total	99.8	31.3) 93.0 d	√ 29.7 _€ (1.7 °	©0.5 €	na na	na	94.7	30.2
Day 7	Methanol extract	3 7.7		66.1	0.5	7:₹ 	0.06	1.9	0.02	73.7	0.60
Day 7 Seed	Acid hydrolysat	10.6 %	0.1	12.2	0.1	L. C	0.02	1.8	0.01	14.1	0.11
	Combinediotal	% 8.5	10 ,8	18 9.3	0,0	256	0.08	na	na	87.8	0.72

Notes:

- All results are means from diplicate samples.
- ppm = mg equivalents of elephon for kg of cample.
- The total radioactive residue (TRR) in the day 0 samples was calculated by summation of the radioactive residues determined in the various fractions (wash extract and fiber). The TRR at Day 7 was determined by combustion.

Conclusion

The metabolism of ¹⁴Cothephon in cotton was investigated after a single application at the rate of 1400 g as/hawhen the plants had reached a growth stage approaching maturity. The radioactive residues in the mature gin trash and seed taken on day 7 after application were principally recovered by extraction with methabol. The remaining radioactivity was recovered by acid hydrolysis, leaving very little radioactive residues bound to fiber. Parent ethephon comprised the main part of the residue in both the gin trash and cotton seed (93.0% and 78.3%, respectively). The metabolite (2-hydroxyethyl)phosphonic acid (HEPA) was present at lower levels representing 1.7% TRR in gin trash and 9.6% TRR in cotton seed.

- General conclusion on the metabolism in crops

The results of the cotton metabolism study are consistent with those of the wheat and tomato metabolism studies. Since wheat, tomato and cotton belong to three different groups in the sense of



the OECD Guideline on metabolism in crops, the results may be generalized to other crop groups, as appropriate. Hence it is concluded that the main degradation route of ethephon in plants involves decomposition to ethylene and phosphates. Ethylene is rapidly released into the atmosphere while the phosphates are taken up in the natural phosphate cycle of the plant. Part of the applied ethephon is metabolized according to a different metabolic pathway that results in the formation of the metabolite (2-hydroxyethyl)phosphonic acid (abbreviated HEPA). HEPA is further metabolized by incorporation of the two carbon atoms in natural bio-molecules.

Figure 6.2.1-1 Metabolism of ethephon in plants

The Annex II dossier of ethephon submitted in 2002 includes to hen metabolism studies in which 8-10 birds per study were dosed or 10 for 5 consecutive days with 14C-ethephon in gelatine capsules at levels equivalent to 53-67 mg/kg in the feed (about 2.6-4.1 mg/kg bw/day). The compound was found to be rapidly and efficiently eliminated in expired oir (mainly as ethylene) and excreta. Less than 1% of the administered radioacticity was recovered in eggs and hen edible tissues.

Characterization of residue constituents in her tissues indicated that besides hydrolysis to ethylene, a competitive degradation pathway results in the formation of the metabolite HEPA, which is likely to be further metabolized via dissociation of the phosphonic acid moiety and incorporation of the carbon atoms into natural tissue constituents such as wids and proteins. Parent ethephon and HEPA accounted for 42% and 14% respectively, of the total radioactive residue (TRR) in kidney, 17% and 16% in liver, and 2% and 18% in muscle. No ethephon or HEPA residues were identified in fat, egg yolk or regg white.

In the EFSA Reasoned opinion on the eview of the existing MRLs for ethephon (EFSA Journal 2009;7(10) 1347) the study was not considered to be necessary since the dietary burden of poultry was estimated to be below the rigger value of 0.1 mg/kg. However, the following conclusions were drawn:

"This study demonstrates that metabolic pathways of ethephon in ruminants and poultry are very similar [...]. It is therefore concluded that the relevant residue in poultry could also be defined as ethephon."



CA 6.2.3 Lactating ruminants

The Annex II dossier of ethephon submitted in 2002 includes a goat metabolism study in which two animals were dosed orally for 7 successive days with ¹⁴C-ethephon in gelatine capsules at a level equivalent to 10 mg/kg in the feed (about 0.37-0.46 mg/kg bw/day). In the EFS Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347) the main study results are summarised as follows:

"This study demonstrates that the parent compound is hydrolysed to lose its chlorine and phosphale groups and that the carbon units are taken up into the tricarboxylic acid cycle to yield natural products like fat, protein, carbohydrate and CO₂. Ethephon and HEPA are expected to be the only toxicologically relevant compounds and the highest radioactive residue level was found in liver (1 mg/kg) of which 0.15% was considered ethephon and/or HEPA (max. 0.0015 mg/kg). [6] Based on these data and the fact that residues in all ruminant demmodities were expected to be very low no residue definition was proposed in the framework of the peer veriew (FFSA, 2008a). In the framework of this review, however, additional crops contribute to the dietary busden of livestock resulting in a higher exposure of livestock to ethephon residues and the necessity to establish a residue definition in pigs and ruminants. Also in contrast to the peer veriew, data are now available indicating that HEPA is expected to result in adverse effects at much higher exposure levels than ethephon [7]. Therefore, the relevant residue in [...] ruminants is now defined as ethernon, both for enforcement and risk assessment purposes."

In the initial peer review process (EFSA Condision, 2008), the goat metabolism study was considered sufficient. To stress the acceptability of this study, the following information is additionally provided.

Residues of ethephon found in all animal matrices were 0.01 mg/kg. The dose administered in goat metabolism study was 40 mg/kg feed (DM) which corresponds to approximately 11 times the maximum concentration taken up through feed items derived from cereals, apples and cotton seed treated according to CGAP of current uses (see EFSA RO, 2009: max. 0.92 mg/kg feed DM). When the maximum residue of 1.08 mg/kg measured in kidney in the goat study is normalised to his feed burden a maximum residue of 1.11 mg/kg results. Of the 0.11 mg/kg radioactive residue only 0.15% is considered to be chephon and/or HEPA (max. 0.00016 mg/kg). Since ethephon residues of less than 0.01 mg/kg is animal edible products are expected with the current GAP no new metabolism studies are deemed newssary. The existing goat ADME study is providing sufficient data regarding the evaluation of the current uses.

In the argumentation (Bayer paper M-223288-02-1(3), P, 2005; KCA 6.2.3/01) further (raw) data from the goal ADME study are presented. 31% of daily dose measured as volatiles on study day 7 is considered representative for the percentage of volatiles in total dose. Characterisation and identification was not considered necessary because residues in tissues and milk were <10% TRR (2.95% and 2.28% respectively).

The metabolism of ethephon has been demonstrated to be both extensive and rapid in goat, hen and

The metabolism of ethephon has been demonstrated to be both extensive and rapid in goat, hen and rat. The metabolic fate of radiolabelled ethephon was, in majority, to be hydrolysed to ethylene and expired via respiration but there was also an additional pathway that lead to the release of ¹⁴CO₂ which was then either be expired of entered the natural biochemical pathways leading to the biosynthesis of amino acids, proteins, carbohydrates and lipids that contain radioactive residues. There was also evidence that gratathione conjugation was an active pathway. It appears that performing an additional goat metabolism study would be very unlikely to add any significant new data to the understanding of the fate of ethephonom ruminants. Thus, acceptance of the existing goat ADME study should be carefully reconsidered, also with regards to animal welfare.

CA 6.2.4 Pigs

According to the EFSA Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347): "Since metabolism in rats and ruminants was demonstrated to be similar,



the findings in ruminants can also be extrapolated to pigs. [...] Therefore, the relevant residue in pigs [...] is now defined as ethephon, both for enforcement and risk assessment purposes."

CA 6.2.5 Fish

No suitable test method for the conduct of metabolism studies on fish is listed in Commission. Communication 2013/C 95/01 about the implementation of Regulation (EU) No 283/2013. Therefore, this point does not need to be addressed at the current stage.

However, according to the working document SANCO/11187/2013 rev. Wit seems that metabolism studies to determine the nature of residues in fish will only be required for far-soluble obstances (log Pow \geq 3). Since ethephon is not a fat-soluble substance its log Pow is extimated to be 189 at pH 7) it is expected that no metabolism study to determine the nature of ethephon derived residues in fish will be required.

CA 6.3 Magnitude of residue trials in plants

The representative uses for the renewal of the approval of etherhon in the EU are defined as a single broadcast spray application to cereals (barley and wheat) to prevent lodging in the context of the renewal dossier the maximum application rate is 480 g as Ma. The latest time for application is BBCH 51 (Beginning of heading: tip of inflorescence emerged from sheath, first spikelet just visible) in the northern residue zone and BBCH 39 (Flog leaf stage: flog leaf tidly unrouled, ligule just visible) in the southern residue zone. Since the application is conducted at an early growth stage, it is not deemed necessary to propose a pre-harvest interval (PHI). These representative uses are the same as the uses that were considered for the previous EV evaluation.

Table 6.3-1: Representative uses of ethephon as an anti-lodging agent in cereals (barley and wheat)

			n	77 P	 	(// n			
Country	F, G, or I	Formur- lation	Method	Gowth Ostage	ication Diterval (days)	Water (L/ha)	Rate (g as/ha)	(days)	Remarks
EU North		SL 3 480 g/L	Folian spraying	BBCP 41-91		200-400	480	1	Since the application is conducted at an early stage, there is no need to set a PHI
EU South		SL 2 480 L	spraying	BB(\$7 3\(\frac{3}{3}\)9	-	200-400	480	-	Since the application is conducted at an early stage, there is no need to set a PHI

A sufficient number of residue trials to support these representative uses are included in the Annex II dossier submitted in 2002. However, in these trials all the straw and grain samples were extracted with methanol, which is not in line with the extraction procedure of the wheat metabolism study. In order to comply with new data requirements [Regulation (EU) No 283/2013) and new guidelines [OECD Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17] it was decided to conduct a new set of trials, in which the straw and grain samples were extracted in the same way as in the wheat metabolism study (i.e. first by blending with methanol and then by digestion with hydrochloric acid).



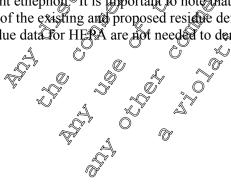
Since ethephon is applied to cereals at an early stage (i.e. before the edible part of the plant forms) and in accordance with the guideline SANCO 7525/VI/95 - rev.9 of March 2011, it possible to extrapolate between barley and wheat. However, as shown in Table 6.3-2, a full set of new trials (8 trials per zone) was conducted for each of the two crops. The trials were distributed over two different growing seasons (2013 and 2014) and half of them were decline trials. Detailed summary ables for these trials may be found in Appendix 1.

Table 6.3-2: Overview of the residue studies conducted to support the representative uses of ethephon as an anti-lodging agent in cereals (barley and wheat)

Crop	Document No.	Report & study No.	Year of trials	Zone	Number of trials	Remarks
Barley	M-526906-01-1	13-2027	2013	North		2 harvest trops and Decline trals
Barley	M-533473-01-1	14-2022	2014	North		harvest trials and 2 decline trials
Barley	M-529491-01-1	13-2028	2013	South	4 🔑	2 harkest trials and 2 dealine trials
Barley	M-533463-01-1	14-2020	2014	South		2 harvest trials and Decline trials
Wheat	M-529493-01-1	13-2029	2013	Morth		harvese trial and 2 decline trials
Wheat	M-532267-01-1	14-2018	2 014	North &	5,0	3 harvest trial and 2 decline trials
Wheat	M-529488-01-1	13-2030	20130	South		2 parvest trials and 2 decline trials
Wheat	M-532272-01-1	14-2019	2014	Søuth		2 harxest trials and 2 decline trials

^{*} In the harvest trials, green material was sampled on day Q and at about growth stage BBCH 75 while grain and straw were sampled at normal harvest. In the decline trials, supplementary samples of green material were taken on about day 7 day 14 and day 21.

In addition to the residues of parent expensive the samples from all the above studies were also analysed for the residues of the metabolite IEPA. However, the available storage stability data for HEPA do not fully cover the storage periods and matrix types of the studies. Furthermore, in several trials, the untreated control samples of grain and straw showed apparent residues of HEPA of about the same magnitude as the residues of HEPA found in the corresponding treated samples. For these reasons, the residue results for HEPA are only considered indicative. In the following summaries they are not commented in detail but nevertheless provided in the result tables next to the residue results for parent ethephon. It is important to note that, due to its favourable toxicological profile, HEPA is not part of the existing and proposed residue definitions for dietary risk assessment or MRL setting. The residue data for HEPA are not needed to demonstrate consumer safety.





CA 6.3.1 Barley

Report: KCA 6.3.1/06; ; 2015; M-526906-@a-1

Title: Determination of the residues of ethephon in/on winter barle@after spray application

of Ethephon SL 480 in Germany, Belgium, the Netherlands and the United Kingdom

Report No.: 13-2027 Document No.: M-526906-01-1

Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 Guideline(s):

October 2009 concerning the placing of plant protection

products on the market and repealing Council Directives 79/117/ERC and

91/414/EEC

EC Guidance working document 7029/VI/95 rev.5 (1/997-07

OECD 509 Adopted 2009-09-07 DECD GO DELINE FOR THE TEST III

eline No. 860.1508 US EPA OCSPP Guideline No. 860

Guideline deviation(s): not specified **GLP/GEP:** yes

Materials and methods

Four residue trials were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in Germany, Belgium, the Netherlands and the United Kingdom. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had beached the growth stage BBCH 51. The treatment was conducted at the target rate of about 480 g as/ha after dilution in 200-300 L/ha of water. In trial however, the application was conducted at the slightly overdosed rate of 512 g as/ha. Samples of green material were taken on day V (shortly after application) and 24-43 days later, at the growth stage BBCH 75. In two grals, additional samples of green material were taken 7, 14 and 21 days after application. In all grals, samples of grain and straw were taken at maturity (BBCH 89), 55-68 days after application.

Details about the design and results of the trials are given in Table 6.3.1-1.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 20 months (582 days) until abalysis. In the Belgian trial (13-2027-02) the temperature rose above -18°C during the shipment of the grown material field samples from the test site to the test facility. The average temperature during shapment was estimated at ca. -11°C. However, owing to the very short duration of the shipment (3 hours and 5 minutes) and since the samples remained frozen, this deviation is unlikely to have impacted the study result.

All the samples were maly self for the Pesidues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the esidues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.



Findings

Table 6.3.1-2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.25.9 mg/kg on day 0 and 6 and decreased to < 0.05-0.43 mg/kg at the growth stage BBCH 75. At harvest, which was 55-88 days after application, the residues of parent ethephon were in the range of 0.067-0.73 mg/kg in grain and 0.35-3.6 mg/kg in straw.

Table 6.3.1-1: Residue trials performed in the northern part of the EU in 2013 to support the use of ethephon as an anti-lodging agent in barley - overview of trial design and residue results [Study 13-2027]

	residue results	•	V	•							
Report	Location	Forn	nulation		Al	plicati	on	Crop Part	Residence (mg/		DALT
Study Trial	Country Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage		GETP 1	PIEPA (Ødays) ∮
M-526906-01-1 13-2027 13-2027-01	2013	SL	480	1	0.48		BBCH &	green material grain	0.51	0.091 0.05 0.05 0.05 0.05 0.013)* 0.013)*	0 7 14 21 24 59
M-526906-01-1 13-2027 13-2027-02	2013	SL	480 8		0.5R	0.19 0.19		green naverial grain	< 0.05 0.067 0.35	<0.05 <0.05 <0.01 <0.05	0 33 55 55
M-526906-01-1 13-2027 13-2027-03	2013	SL Y	4807		\$48		BBCT 51	*green material	7.9 3.8 0.85 0.57 0.27	0.094 0.088 0.085 0.076 0.059	0 7 14 21 43
M-526906-01-1		CIA	480	\(\sum_{1}^{\text{0}}			BBCH 51	straw	1.5	< 0.05	56
13-2027 13-2027-04		SK	48V	ı		0.24	рвси 31	green material grain	0.36	0.093< 0.050.055	34 68
Ş	20.130	0		y	Z	y		straw	3.6	0.066	68

* If \(\geq \text{LOQ}, \text{the residues found in the corresponding control sample are shown in brackets.} \)
The residues of parent thephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

DALT: days after last treatment
ETP: ethephon; HEPA: phydroxy ethyl-phosphonic acid.
* If \ge LOQ, the residue found in the corresponding control sample are shown in brackets.

Table 6.3.1- 2: Validation data and concurrent recoveries for the determination of ethephonderived residues in cereal commodities from the 2013 season residue trials [Studies 13-2027, 13-2028, 13-2029 & 13-2030]

Report (Method)	Matrix	Compound	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries	Mean recovery [%]	RSD [%]
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1 (01429)	Green material	Ethephon	0.05 0.5 5.0 10 20 overall	5 4 1 3 1 140	81; 108; 16; 87; 94 78; 106; 78; 95 700 81; 89; 82	97 \$9 100 & 84 & \$1	105 +5.4 - 5.2 - - 13.8
		НЕРА	0.05 0.5 5.0 10 20 overal	140 5 4 % 1 3 %	93; 102; 112; 97, 113 84, 105; 74; 98 94 82; 83; 84 76	103 © 90 84 © 76 93	8.6 16.9 - 1.8 - 13.9
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1 (01429)	Grain	Ethephon	001 00.1 01.0 0 verall	3 V 2 V 27 X	96; 110; 81 95, 101 90; 91	96 98 91 95	15.2 - - 9.6
		HEPA	001 0.1 1.0 overall		105; 93, 102 86, 104 90; 85	100 93 83 93	6.2 - - 11.8
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1' (01429)	Straw ,	Ethephon	0.05 0.5 5.0 0.5 0.5 0.5 0.5		92; 99 86; 85 89; 91	96 86 90 90	- - - 5.6
		HEPA	0.5 0.5 5,0 overall	Q 4 _Q	80; 86; 99; 103 70; 77 80; 78	92 74 79 84	11.7 - - 13.5

The fortification levels are expressed as ether on for parent ether on and as HEPA for the metabolite HEPA.

Conclusion

Four residue thats were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. In each trial there was one foliar application at the tate of \$60-512 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 55-68 days ofter application, the residues of parent ethephon were in the range of 0.067-0.73 mg/kg in grain and 0.35-3.6 mg/kg in straw.



Report: KCA 6.3.1/07; ; 2015; M-533473-01-1

Title: Determination of the residues of ethephon in/on winter barley after spray application

of ethephon SL 480 in Germany, northern France and the United Kingdom

Report No.: 14-2022 Document No.: M-533473-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21

October 2009 concerning the placing of plant protection products on the market; OECD Guideline for the Testing of Chemicals on Crop Field Trial TG 500 published in September 2009); US EPA OCSPP Guideline No. 860/1500 or Crop Field Trial

Guideline deviation(s): none **GLP/GEP:** yes

Materials and methods

Four residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in Germany, France and the United Kingdom. In such trial the product Ethephon 50 480 get was applied once as a broadcast foliar spray, usually when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of about 480 g as to after dilution in 200-336 L/ha of water. In one trial, however, the application was belayed intil the growth stage BBCH 55, while in an other trial the application was conducted at the slightly overdosed rate of 537 g as/ha. Samples of green material were aken or day 0 (shortly after application) and 21-36 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 56-78 days after application.

Details about the design and results of the trials are given in Vable (3).1-3.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 14 months (414 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX)5 μ m, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and when samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 6.2-7.7 mg/kg on day 0 and had decreased to < 0.05-0.37 mg/kg at the growth stage BBCH 75. At harvest, which was 56-78 days after application, the residues of parent ethephon were in the range of 0.031-0.41 mg/kg in grain and 0.43-1.2 mg/kg in straw.

Table 6.3.1-3: Residue trials performed in the northern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in barley - overview of trial design and residue results [Study 14-2022]

Report Study	Location	Formulation		Application			Zop (Residues (mg/kg)		
Trial	Country Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage	Spart &	ETP	HEPA	(days)
M-533473-01-1 14-2022 14-2022-01	2014	SL	480	1	0.54	0.16 2	BBCH 51	green material	€6.2 ©0.50 0.29	*0,12 \$\alpha\$ 0.05 \$\leq 0.05	0 7 14
								grain	0.086	< 0.05 < 0.05 \display 0.016	21 36 78
					*			straw	0.64	0.055	78
M-533473-01-1 14-2022	,	SL	480 0) 1	0.48/ Sy	0.16	BBCH 31	green n@terial	0.37	0.12 < 0.05	0 21
14-2022-02	2014			G,		Ç j		y grain	0.41	0.055 (0.054)*	64
		Č Š)				straw	1.2	0.063 (0.061)*	64
M-533473-01-1 14-2022		SL.	\$\frac{2}{80}	Ó	0.48	0.16	BOCH 54	green material	6.6 0.34	< 0.05 < 0.05	0 7
14-2022-03	2014			•	Z				0.15 0.10	< 0.05 < 0.05	14 21
	2014	W [¥]		, C					< 0.05	< 0.05	28
		, (Ĉ		>	Q,	Ď	7	grain	0.090	0.021	56
				0) ^v	S,		straw	0.43	< 0.05	56
M-533473-01-1 % 14-2022		ØŠL	38 0	f×	0.48	0.24	BBCH 55	green material	7.3 0.13	0.072 0.050	0 34
14-2022-04		Ö W		, S	¥ *V*			grain	0.16	0.047 (0.011)*	73
	2014			>				straw	0.78 (0.088)*	< 0.05	73

DALT : days after las treatment

ETP: ether hon; HEPA: 2 hydroxy-ethyl-phosphonic acid.

* If \(\) \(\) \(\) \(\) the esidues found in the corresponding control sample are shown in brackets.

The residues of parent etherhon are expressed as etherhon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.



Table 6.3.1- 4: Validation data and concurrent recoveries for the determination of ethephonderived residues in cereal commodities from the 2014 season residue trials [Studies 14-2018, 14-2019, 14-2020 & 14-2022]

Report (Method)	Matrix	Compound	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries	Mean recovery	RSD [%]
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Green material	Ethephon	0.05 0.50 5.0 10 20 overall	6 4 1 3 1 150	99; 100; 100; \$7; 94; \$01 89; 90; 94 89; 90; 94 92; 87; 88	97 93 89 89 89 89 89	5% 4.0 - 3.0 - - - - 5.5
		НЕРА	0.05 0.50 5.0 10 20 overal	\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	96 91: 78; 90 91: 78; 90 91: 700 91: 700	94 8 85 86 100 90	8.4 5.4 - 9.8 - 8.7
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Grain	Ethephon	901 0.10 1.0 0 overall	0 4 0 2 4 0 4 0 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	\$65; 109; 100; 109 \$65, 106 \$76; 90 \$76; 90	106 98 94 101	4.0 - - 7.9
		HEPA	001 0.10 1.0 overall		85; 96, 90 85, 82 97; 82	90 84 81 86	6.1 - - 6.7
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Straw	Ethephon	0,05 0,50 0.50 1.5 5 0,000 0,000 1.5	0' 5 0 0' 5 0 1 13	93, 108; 113; 83; 104 90; 100; 103; 106 70; 70; 80 71	100 100 73 - 92	12.1 7.0 7.9 - 16.8
		HEPA	0.05 0.500 1.57 5.0 (overall	3 1 12	73; 82; 106; 77 63; 71; 83; 70 66; 68; 77 66	85 72 70 - 75	17.5 11.6 8.3 - 15.4

The fortification levels are expressed as Thephon Por parent ethephon and as HEPA for the metabolite HEPA.

Conclusion

Four residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of experion as an anti-lodging agent in barley. In each trial there was one foliar application at the rate of 480-537 g as/ha when the crop had reached the growth stage BBCH 51, except in one trial, in which the application was delayed until the growth stage BBCH 55. At harvest, which was 56-78 days after application, the residues of parent ethephon were in the range of 0.031-0.41 mg/kg in grain and 0.43-1.2 mg/kg in straw.

^{*} This recovery was corrected for the apparent residue of 0.0165 mg/kg in the control sample used for fortification. Before correction the recovery was 122%.



Report: KCA 6.3.1/08; 2015; M-529491-01-1

Title: Determination of the residues of ethephon in/on winter barley after spray application

of ethephon SL 480 in southern France, Spain and Italy

Report No.: 13-2028 M-529491-01-1 Document No.:

Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 Guideline(s):

October 2009 concerning the placing of plant protection products on the market and

repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1992)207-2

OECD 509 Adopted 2009-09-07, OECD Guideline for the testing of Chemicals Crop

Field Trial

US EPA OCSPP Guideline No. 860.150

Guideline deviation(s): not specified

GLP/GEP:

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barles. The trial sites were located in France, Spain and Italy. In each trial the product shephon \$L 4800 L was applied once and broadcast foliar spray when the crop had reached the growth stage BBCI139. The treatment was conducted at the target rate of 480 g as/ha after dilution of 300 400 L/ha of water. Samples of geen material were taken on day 0 (shortly after application) and 24-39 days later at the growth stage BBCH 75. In two trials, additional samples of green material, were taken 7, 12-14 and 21 days, after application. In all trials, samples of grain and straw were taken at rhaturity (BBCH Q9), 62-72 days after application.

Details about the design and results of the trials are given in Table 6.3.1-5.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 22 months (647 days) until analysis. In the French and Spanish treals (13-2028-01 and 13-2028-02, respectively) the temperature rose above 18°C during the shipment of the green material field samples from the respective test site to the test facility." The werage temperature during shipment was estimated at -15.6°C and \$13.5°C, respectively. However, owing to the relatively short duration of the shipment (less than 21/16/urs in the French trial; day and 5 hours in the Spanish trial) and since the samples remained frozen, this deviation is unlikely to have significantly impacted the study results.

All the samples were applysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and graw the residues were extracted by blending three times with methanol followed by digestion with a prixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna Sex 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1-2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.



The residues of parent ethephon in green material were in the range of 3.5-5.9 mg/kg on day 0 and had decreased to < 0.05-0.26 mg/kg at the growth stage BBCH 75. At harvest, which was 62-72 days after application, the residues of parent ethephon were in the range of 0.021-0.21 mg/kg in grain and 0.23-1.7 mg/kg in straw.

Residue trials performed in the southern part of the Eldin 2018 to support the **Table 6.3.1-5:** use of ethephon as an anti-lodging agent in barley - overview of trial design and residue results [Study 13-2028]

Report	Location Country	Forn	nulation		Aj	opheati	~ · · · · · · ·	Crop	Resi (mg	dues Jkg)	DALT
Study Trial	Year	Туре	Content g/L	No	h(a)	kg as/ hL	≓ ctao@?າ	part	E	HEPÄ	(days)
M-529491-01-1 13-2028 13-2028-01	2013	SL	480		Q 48 Q 2			y grain	0.15° 0092 < 0.05	©0.053 < 0.05 < 0.05 < 0.05 < 0.05 < 0.01 < 0.05	0 7 12 21 39 71
M-529491-01-1 13-2028 13-2028-02	2013	SL Y	4807		Q.48	0(<u>1)</u> 2	BBOH 39	Pareen material grain	4.2 0.26 0.21	0.058 (0.081)* < 0.05 0.069 (0.023)*	0 27 72
M-529491-01-1 13-2028	2013	SK	4800	1	10 A 8	0.40	BBCH 39	green material	5.9 0.44	0.17 (0.17)* 0.051 < 0.05	72 0 7
13-2028-03	2013	\$ *\diagram \text{\te}\tint{\texi}\text{\text{\texi}\text{\text{\text{\text{\texi{\text{\texi{\texi\texi{\texi}\\ \text{\texi}\tinz}\\ \texit{\text{\texi{\texi{\texi{\texi{\texi{\texi{\t		y		7 0			0.087 0.078 0.051	< 0.05 < 0.05 < 0.05	14 21 24
, C			Ű,		7			grain straw	0.041	0.012 0.054	62
M-529491-0 13-2028 13-2028-0-4	2013		4800	1	0.48	0.14	BBCH 39	green material grain	3.5 < 0.05 0.021	<0.05 <0.05 0.070 (0.060)*	0 29 64
								straw	0.24	< 0.05	64

DALT: days after last treatment ETP: ethephon; MEPA: 2-hydroxy-ethyl-phosphonic acid.

The residues of parencethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

^{*} If \geq LOQ, the residues found in the corresponding control sample are shown in brackets.



Conclusion

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 62-72 days after application, the residues of parent ethephon were in the range of 0.021-0.21 mg/kg in grain and 0.23-1.7 mg/kg in straw.

Report: KCA 6.3.1/09; ; 2013, M-583,463-016

Title: Determination of the residues of ethephon in/on winter barley after spray application

of ethephon SL 480 in southern France, Spain, Paly and Greece

Report No.: 14-2020 Document No.: M-533463-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the Eucopean Parliament and of the Coupear of 21

October 2009 concerning the placing of plant protection products on the market; OECD Guideline for the Testing of Chemicals on Crop Field Thal (TG 499 published in September 2009); USEPA OCSEP Guideline No. 60.1500 on Crop Field Trial

Guideline deviation(s): none GLP/GEP: yes

Materials and methods

Four residue trials were conducted in the couthern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in France, Spain, Italy and Greece. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray, usually when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of about 480 g as ha after dilution in 300-400 L/ha of water. In one trial, however, the application was delayed until the growth stage BBCH 43 and conducted at the under-dosed rate of 40 g as/ha. Samples of green material were taken on day 0 (shortly after application) and 29 48 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 6-7, 14 and 20 3 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89) 63-72 days after application.

Details about the design and results of the trials are given in Table 6.3.1-6.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 15 months (427 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luña SCX 5 μ m, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1-4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.3 2 mg/kg on day 0 and bad decreased to < 0.05-0.36 mg/kg at the growth stage BBCH 75. At harvest, which was 63=1/2 days after application, the residues of parent ethephon were in the range of 0.034-0.14 mg/kg in grain and 0.35-1.1 mg/kg in straw.

Table 6.3.1- 6: Residue trials performed in the southern part of the EU in 2014 to Sipport the use of ethephon as an anti-lodging agent in barley overview of trial design and residue results [Study 14-2020]

					*	\bigcap^{γ}		(,	9		
Report Study	Location Country	Forn	nulation ~	Z Z		plicati		Cropp	Rosi Ing	dues /kg)	DALT
Trial	Year	Туре	Content	No	kg as/	kg@s/ HL	Growth		©ETP	НЕРА	(days)
M-533463-01-1	0	SL (480	P	0.48	0.16	ввсн39	green material	5.6	0.069	0
14-2020		Ĉ)		. Ô		material	3.0	0.055	7
14-2020-01		Ò	\\ \\ \\ \'		~ ~~				3.0	0.055	14
	2014	V		a.		à		7	0.38	< 0.05	21
	√.			J	. «	\$			0.095	< 0.05	42
				ħ				grain	0.14	0.026	72
	Ų	aR'	Ö		٧.	W		straw	1.1	< 0.05	72
M-533463-01-1		øSL	480 ×	, 1	0.45	0.12	BBCH 43	green	6.6	0.14	0
14-2020	*		ř)	Q,		,	material	0.36	< 0.05	29
14-2020-02	2014 (7)			0	57"	T		grain	0.039	0.013	64
9/		Q~		Q		<i></i> ₽ _Л					
				y				straw	0.97	0.080	64
M-533463-01-1		SL	480%	1 🖔	0.48	0.12	BBCH 39	green	3.3	< 0.05	0
14-2020	2014	\(\tau_{0} \)			¥			material	1.2	< 0.05	6
14-2020-03			Ŵ,						0.34	< 0.05	14
14-2020-03				7					0.10	< 0.05	20
O*		1.0							< 0.05	< 0.05	29
		Ű						grain	0.047	< 0.01	64
			Ÿ					straw	0.39	< 0.05	64
M-533463-04A		SLY	480	1	0.48	0.16	BBCH 39	green	8.2	0.14	0
14-2020	Ž014							material	< 0.05	< 0.05	48
14-2020-04		ď						grain	0.034	0.014	63
								straw	0.35	< 0.05	63

DALT: days after last treatment

ETP: ethephon; HEPA: 2-hydroxy-ethyl-phosphonic acid.

The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.



Conclusion

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. In three trials there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. In the fourth trial the application was delayed until the growth stage BBCH 43 and conducted at the rate of 411 g as/ha. At harvest, which was 63-72 days after application, the residues of parent ethephon were in the range of 0.034-0.14 mg/kg in grain and 0.35-1.1 mg/kg in straw.

CA 6.3.2 Wheat

Report: KCA 6.3.2/06; ; ; ; 2015; M\$29492-01-1

Title: Determination of the residues of ether from in/on soft wheat after pray application of

ethephon SL 480 in Germany, Belgum and the United Kingdom

Report No.: 13-2029 Document No.: M-529493-01-1

Guideline(s): Regulation (EC) No.1.107/2009 of the Guropean Parliament and 66 the Council of 21

October 2009 concerning the placing of plan@rotection products on the market and

repealing Council Directives 79/117/EEC and 91/41 PEEC EC Guidance working document 9029/V 95 rev 5 1997-07-22)

OECD 509 Adopted 2009-09-07, OECD Guideline for the testing of Chemicals, Crop

Field Trial

US EPA OCSPR Quideline No. 860, 1500

Guideline deviation(s): not specified **GLP/GEP:** ves

Materials and methods

Three residue trials were conducted in the porthern part of Europe during the 2013 growing season to support the use of ethephon as an anti-ledging agent in wheat. The trial sites were located in Germany, Bergium and the United Kingdom. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of 480 gas/ha after dilution in 200-300 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 23-38 days later, at the growth stage BBCH 75-77. In two trials, additional samples of green material were taken 7-8, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 61-75 days after application.

Details about the design and results of the trials are given in Table 6.3.2-1.

The samples were frozen within 24 hours of sampling and stored deep frozen for a maximum of 20 months (60 ways) until analysis. In the Belgian trial (13-2029-02) the temperature rose above -18°C during the shipment of the day 0, day 8 and day 14 green material field samples from the test site to the test facility. The average temperature during shipment was estimated at ca. -11°C. However, owing to the very short duration of the shipment (3 hours and 5 minutes) and since the samples remained frozen, this deviation is unlikely to have impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by



digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw an 0.01 mg/kg in/on cereal grain.

recoveries determined and studies conducted in Parents (and fortification accuracy) of the residue reference.

Aterial were in the range of 3.1-78, mg/kg in stage BBCH 75. At parcent, which was 6 and were in the range of 0.059-0.11 mg/kg in grant of the residue reference. Table 6.3.1- 2 provides an overview of the procedural recovered determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within .

The residues of parent ethephon in green material were in the range of 3.1-7.5 mg/kg on day and had decreased to 0.11-0.32 mg/kg at the growth stage BBCH 75. At hawest, which was 61-75 days after application, the residues of parent ethephon were in the range of 0.059-001 mg/kg in grain and

Residue trials performed in the northern part of the EU in 2013 to support the Table 6.3.2- 1: use of ethephon as an anti-lodging agent in wheat - overview of trial design and residue results [Study 13-2029]

Report	Location Formulation Country			Aj	pplicati	on	Crop part	Resi (mg	/kg)	DALT	
Study Trial	Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage		1		(days)
M-529493-01-1 13-2029		SL	480	1	0.48	0.16	BBCH 5	mangijai	0(4)6	< 0.05 < 0.05	0 7
13-2029-01	2013							. ~ ~	9/21 0.17	0.05	14
					X	D O			0.17	< 0.05	23
							, <u>a</u>	grain	0.059	0 0 27	75 75
					Q,	\\\\		h .	0 .36	(0.030	/3
M-529493-01-1		SL	480	1	0.48	9 0.16	BBCH 51	green	3.1	< 0.05	0
13-2029	2013		8		Q,			material	0. © © 1	< 0.05	8
13-2029-02				9	L, '	S	W	. W	091 @₁0.11	< 0.05 < 0.05	14 21
				(0 11	< 0.05	29
		<i>(</i>	D* /	\$, Q			gra@n	0.059	0.029	61
		۵						%straw	0.66	< 0.05	61
M-529493-01-1	*	S L	\$80	Ł	0.48	0.24	PB CH 51	green	7.5	0.076	0
13-2029	0			Ő	· ~/ /			material	0.32	0.050	38
13-2029-03	2012			n				grain	0.11	0.080	74
	2013	Ź	Ž,		Y é	<u></u>		straw	1.3	0.083	74

DALT : days after last treatment

ETP: ethephon; HEPA 2-hydroxy-ethy phosphoric acid?
The residues of parenthanks The residues of parent ethephor are expressed a ethephor and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for die ary risk assessment or MRL setting.

Conclusion

Three residue that's were conducted in the northern part of Europe during the 2013 growing season to support the use of etherhon as an anti-odging agent in wheat. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 61-75 days after application, the residues of parent ethephon were in the range of 0.059 of 1 mg/kg in gram and 0.36-1.3 mg/kg in straw. and 0, 36-1.3



Report: KCA 6.3.2/07; ; 2015; M-532267-01-1

Title: Determination of the residues of ethephon in/on winter wheat after spray application

of ethephon SL 480 in Germany, the United Kingdom, northern France and the

Netherlands

Report No.: 14-2018 Document No.: M-532267-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21

October 2009 concerning the placing of plant protection products on the market OECD Guideline for the Testing of Chemicals on Crop Field Tital (TG 509 published

in September 2009)

US EPA OCSPP Guideline No. 860.1500 on Crop Field Triss

Guideline deviation(s): not specified

GLP/GEP: yes

Materials and methods

Five residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat of he trial sites were located in Germany, the United Kingdom, France and the Netherlands on each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar sprow when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of 480 g as/ha after didution in 200-400 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 26-36 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7-8, 14-15 and 21-22 days after application. In all trials, samples of grein and straw were taken at maturity (BBCH 89), 54-77 days after application.

Details about the design and results of the trials are given in Pable 6 3.2-2.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 10 months (296 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically Jabelle Linternal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Linia SCX) µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and when samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 4.9-7.2 mg/kg on day 0 and had decreased to 0.071-0.23 mg/kg at the growth stage BBCH 75. At harvest, which was 54-77 days after application, the residues of parent ethephon were in the range of 0.052-0.31 mg/kg in grain and 0.44-1.5 mg/kg in straw.



Table 6.3.2- 2: Residue trials performed in the northern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in wheat - overview of trial design and residue results [Study 14-2018]

Report Study	Location Country	Forn	nulation		Aj	plicati	on	Top	Residence (mg	/kg)	Ø ALT
Trial	Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL _{∕≥}	Growth stage	Spart &	ETP	НЕРЖ	(days)
M-532267-01-1 14-2018		SL	480	1	0.48	0.16	BBCH,51	green material	7.9 70.28	9,085 \$4,0.05	0 8
14-2018-01	2014								0.29 0.25 0.22	0.05 < 0.05 < 0.05	° 14 21 29
				2				grain		©0.031 (0.013)*	71
			**		Ŷ Q			straw	0.44	< 0.05	71
M-532267-01-1 14-2018	2014	SL	480	1	,0 ,48	0 <i>0</i> 6	BB C H 51	green material	$\mathbb{Z}_{0.23}^{7.0}$	0.078 < 0.05	0 26
14-2018-02		(Ş		* _C		grain	0.14	0.040	68
	٠	S S				Ö'		straw	1.2	0.15 (0.23)*	68
M-532267-01-1 14-2018 14-2018-03		∜SL .	3 780		0.48	0.24	BBCH 54	green material	7.0 0.39 0.27	0.073 < 0.05 < 0.05	0 7 15
14-2010-03	2014		Ö	C	Y	W D			0.27 0.17 0.12	< 0.05 < 0.05 < 0.05	22 36
		Á						grain	0.23	0.089 (0.043)*	64
•		\$\frac{10^{2}}{10^{2}}.	Ď	Ĺ		,		straw	1.2	0.055	64
M-532267-01-4C14-2018	2	SL	480 ^	yl	0.48	0.16	BBCH 51	green material	7.2 0.071	0.087 < 0.05	0 35
14-2018-04	2014	W			V			grain	0.052	0.019	77
) ·	Ů,					straw	0.57	< 0.05	77
M-532267-0		SIÇ	4800	1	0.48	0.12	BBCH 51	green material	5.9 0.23	0.062 < 0.05	0 32
14-2018-03,	2014							grain	0.31	0.046	54
¥ Ş)					straw	1.5	< 0.05	54

DALT : days after last treatment

The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Five residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar

ETP: ethephon; HCPA: 2-hydroxy-ethyl-phosphonic acid. * If \geq LOQ, the residues found in the corresponding control sample are shown in brackets.



application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 54-77 days after application, the residues of parent ethephon were in the range of 0.052-0.31 mg/kg in grain and 0.44-1.5 mg/kg in straw.

Report: KCA 6.3.2/08; : 2015: M-529488-01-1

Title: Determination of the residues of ethephon in/on soft wheat after spray application of

ethephon SL 480 in southern France, Spain and Italy

Report No.: Document No.: M-529488-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21

October 2009 concerning the placing of plant profection products on the market and

repealing Council Directives 79/117 EC and 91/414 SEC

EC Guidance working document 7029/VI/95 tev.5 (1997-07,22)

OECD 509 Adopted 2009-09-07 DECD Guideling for the lesting of themicals, Crop

Field Trial

US EPA OCSPP Guideline No. 860, 1500

not specified Guideline deviation(s): **GLP/GEP:** yes

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. The trial sites were located in France, Spain and Italy. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of about 480 g as a after dilution in 300-350 L/hazof water. In one trial, however, the application was conducted at the spently werdosed rate of 515 gras ha. Samples of green material were taken on day 0 (shortly after application) and 24-45 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, and 21 days after application. In all trials, samples of gram and straw were taken at maturity (BREH 89), 62-80 days after application.

Details about the design and results of the trials are given in Table 6.3.2-3.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 24 months (713 days) until analysis.

All the samples were maly sed for the esidue of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and strain the residues were extracted by blending three times with methanol followed by digestion with a mixtur of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an sotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (exchange column (exchange Luna Sex 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.00 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1-2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 5.6-17 mg/kg on day 0 and had decreased to 0.05-0.21 mg/kg at the growth stage BBCH 75. At harvest, which was 62-80 days after application, the residues of parent ethephon were in the range of 0.10-0.13 mg/kg in grain and 0.30-1.7 mg/kg in straw.

Table 6.3.2- 3: Residue trials performed in the southern part of the 10 in 2013 to support the use of ethephon as an anti-lodging agent in wheat -overview of trial design and residue results [Study 13-2030]

						- 54. /		C Y	<i>∞</i> ′	<u> </u>	
Report	Location	Forn	nulation			policati	on'y	Crop	Resi	dues /kg)	DALT
Study Trial	Country Year	Туре	Content g/L	No	kg Qs/ OMa	kg a⊗	4 15/2 4 15/2	port	ETP	ÆEPA Ü	(days)
M-529488-01-1 13-2030		SL	480		0.48 <u></u>	9 0.16	BECH 39	green smaterial	0.50	< 0.05	0 7
132030-01				ď	, ~~	Q	.// .	Ö	90x1	< 0.05	14
	2013				4			4 .)	$^{0.24}$	< 0.05	21
)	Ç			0.16	< 0.05	45
		اع ا		Ş				grain	0.049	0.037 (0.017)*	80
	9	Ö		,	\sim	Ö		straw	0.86	0.051	80
M-529488-01-1		SL ·	¥80	AV	0.52	0.16	₿ ₿ СН ३ ९	green	17	0.24	0
13-2030		,0) }	°~			material	0.21	< 0.05	43
132030-02	2013		Ö	ني ا	Ş	W W		grain	0.057	0.029	64
		<i>V</i>			Į.		\$	straw	0.84	< 0.05	64
M-529488-01-1		SL	¥ 480 Å	<i>y</i> 1	0,48	0.16	BBCH 39	green	6.9	< 0.05	0
13-2030	2019	4	/ 480 G		ZY	Ş		material	0.48	< 0.05	7
132030-03		000		Ć					0.17	< 0.05	14
9/		~	LÕ,						0.19	< 0.05	21
				y					0.16	< 0.05	24
	2019	<i>_</i>		(. *			grain	0.13	0.044	63
			4	Ő	¥			straw	1.7	0.12	63
M-529488-01-1		SL &	\$\frac{480}{480}	≫ 1	0.48	0.14	BBCH 39	green	5.6	0.11	0
13-2030	2013			ľ				material	0.050	< 0.05	25
132030-04		Ů						grain	0.010	0.014	62
		(Y					straw	0.30	0.058	62

DALT : days after last treatment

ETP: ethephon; HEPA: 2-hodroxy-ethyl-phosphonic acid.

The residues of parent expensed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar

^{*} If \geq LOQ, the residues found in the corresponding control sample are shown in brackets.



application at the rate of 480-515 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 62-80 days after application, the residues of parent ethephon were in the range of 0.10-0.13 mg/kg in grain and 0.30-1.7 mg/kg in straw.

Report: KCA 6.3.2/09; 2015; M-5322Q2-01-1

Title: Determination of the residues of ethephon in/on winter wheat after spray apprication

of ethephon SL 480 in southern France, Spain, Italy and Portugal

Report No.: 14-2019 Document No.: M-532272-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21

> October 2009 concerning the placing of plant profection products on the market OECD Guideline for the Testing of premicals on Crop Field Trial (TG, 509 published in September 2009)
>
> US EPA OCSPP Guideline No. 600.1500 on Crop Field Trial
> not specified
> yes October 2009 concerning the placing of plant profection products on the market

Guideline deviation(s):

GLP/GEP:

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-Odging gent in wheat The trial sites were located in France, Spain, Italy and Portugal. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of 480 g as har after didution for 300-400 L/har of water. Samples of green material were taken on day 0 (shortly after application) and 30 60 days fater, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, comples of grain and straw were taken at maturity (BBCH 89), 58-110 days after application.

Details about the design and results of the totals are given in Table 6.3.2-4.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 13 months (384 days) unity analysis. In the French trial (14-2019-01) the temperature rose above -18°C during the shipment of the day 0, day 7, day 14 and day 21 green material field samples from the test site to the test facility. The average temperature during shipment was estimated at ca. -16.7°C. However, owing to the relatively sport duration of the shipment (1 day and 6 hours) and since the samples remained frozen, this deviation is unlikely to have significantly impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1-4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The



average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 6.4-16 mg/kg on day 0 and had decreased to < 0.05-0.26 mg/kg at the growth stage BBCH 75. At harvest, which was 58-110 days after application, the residues of parent ethephon were in the range of 0.011-0.40 mg/kg in grain and 0.21-1.2 mg/kg in straw.

Table 6.3.2- 4: Residue trials performed in the southern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in wheat – overview of trial design and residue results [Study 14-2019]

F					\mathcal{A}					\sim	
Report Study	Location Country	Form	nulation		~ "	pplicate	. •	©fop (Resi (mg	dues Č	DALT
Trial	Year	Туре	Content g/L	No O	kg ask ha 🍣	tog as∕ ∤ hL	Growth Stage	10°	ETPC	НЕРА	(days)
M-532272-01-1 14-2019		SL	480) 1	0.48	0.10	BBCH 39	green material	©1″ ©0.27	0.13 < 0.05	0 7
14-2019-01	2014			(D" *	Ç,		y S	0.16	< 0.05 < 0.05	14 21
		Ĉ							< 0.12	< 0.05	41
	\$			4	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Ö d		grain	0.025	0.019 (0.015)*	77
	₩	·		O ^y	~\ 	Ò		straw	0.29	0.079	77
M-532272-01-1 14-2019	2014		480	1	0.48	0.16 Ø	BBCH 39	green material	6.4 < 0.05	0.087 < 0.05	0 39
14-2019-02	2014	, , Q						grain	0.011	0.019 (0.023)*	72
%				Ç	\$ ⁷			straw	0.21	0.092 (0.12)*	72
M-532272-01	2014	SL	9 480	% 1	0,78	0.12	BBCH 39	green material	10 0.82	0.12 < 0.05	0 7
14-2019-03				Ş	¥			material	0.30	< 0.05	14
				>					0.30 0.26	< 0.05 < 0.05	21 30
				V				grain	0.10	0.042	58
		O						straw	1.2	< 0.05	58
M-53272-01-1@ 14-2019	~ ()	SL	7480	1	0.48	0.16	BBCH 39	green material	16 0.075	0.21 < 0.05	0 60
14-2019-04	2014	j Ž						grain	0.043	0.031 (0.029)*	110
								straw	0.44	0.084 (0.061)*	110

DALT: days after last treatment

ETP: ethephon; HEPA: 2-hydroxy-ethyl-phosphonic acid.

The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

^{*} If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 58-110 days after application, the residues of parent ethephon were in the range of 0.011-0.10 mg/kg in grain and 0.21-1.2 mg/kg in straw.

CA 6.4 Feeding studies

The maximum and mean dietary exposures of livestock of ethephon residues were estimated according to the feed consumption data and principles outlined in the OFOD Guidance Document on Residues in Livestock [ENV/JM/MONO(2013)8]. The feed confinodities and residue levels taken into account are listed in Table 6.4-1. The estimated maximum and mean dietary exposures are shown in Table 6.4-2 and Table 6.4-3, respectively. Since the exposure estimates for both cattle and goultry exceed the trigger of 0.004 mg/kg bw/day, livestock metabolism and livestock feeding studies to investigate the nature and magnitude of ethephon-derived residues in food of animal originare needed.

Table 6.4-1: Feed commodities and residue levels considered to estimate the dietary exposure of livestock

	√ ∧	
Crop and commodity	Residue level@sed for maximum / mean dietay Lourden adculation Mag/kg	Comment
Barley straw	3.6 / 0.1	HR and STMR based on the dataset for the northern part of the Edy. Refer to CA 6.7.2.
Wheat straw	\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	and som Based on the dataset for the southern and northern part of the EU, respectively. Refer to CA 6.7.2.
Barley grain	\$ Q5 \$	STMR based on the dataset for the northern part of the L.D. Refer to CA 6.7.2.
Wheat grain	0.10	STMR based on the dataset for the northern part of the EU. Refer to CA 6.7.2.
Brewer's gram (dried)	\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	STMR from the northern part of the EU (0.15 mg/kg) x median processing factor for brewers grain (0.06).
Distiller's grain (dried)		No processing data for distiller's grain are available but this does not impact the outcome of the calculation since in the group of by-product commodities only one commodity is selected for calculation and "wheat milled by-products" is expected to provide the worst case both in terms of residue levels and in terms of the amounts fed to livestock.
Wheat gluten meal	0.01	STMR from the northern part of the EU (0.10 mg/kg) x median processing factor for wheat gluten meal (0.1).
Wheat milled by- products	0.32	STMR from the northern part of the EU (0.10 mg/kg) x mean processing factor for shorts (3.2). Shorts were chosen to represent "wheat milled by-products" since they represent the worst case in terms of processing



factor compared to bran, germs or middlings.

Table 6.4-2: Maximum dietary exposure of livestock to parent ethephon residues in Europe

Licente de catacame	Maximum die	tary exposure	Trigger
Livestock category	(mg/kg bw/day)	(mg/kg DM)	Maximum contributing commodity exceeded (Y/N)
Cattle - Beef	0.033	1.39	Barley straw
Cattle - Dairy	0.053	1.39	Barley straw of T
Sheep - ram/ewe	0.086	2.57	Barley straw S Y Y Y
Sheep - lamb	0.109	2.57	Barle Straw Y Y Y
Swine - breeding	0.006	0.267	Wheat milled by-products
Swine - finishing	0.008	0.267	Wheat mulfed by in roducts Y
Poultry - broiler	0.014	0.192	Wheat milled by products Y
Poultry - layer	0.028	0.403	Barley stray Y
Poultry - turkey	0.011	0.458	Wheat miled by products Y

Table 6.4-3: Median dietary exposure of divestock to parent etherhon residues in Europe

Livestock category	Median dieta (mg/kg bw/day)	ary exposire (mg/kg DM)	Maximum contributing commodity	Trigger exceeded (Y/N)
Cattle - Beef	0.016	0.41	Barley ştraw	Y
Cattle - Dairy	00016	L ~ S	Barley straw	Y
Sheep - ram/ewe	Ø.021 L	0.624	Barley straw	Y
Sheep - lamb	0.027	0.62	Parley straw	Y
Swine - breeding	O 0.4996	0.267	Wheat willed by-products	Y
Swine - finishing	∑ 9 .008 ♥	267 Q	Wheat milled by-products	Y
Poultry - broiler	\$\infty 0.01\$\forall \(\sigma \)	0.1927	Wheat milled by-products	Y
Poultry - layer 🛸	0.020	0,298	Wheat straw	Y
Poultry - turkey	0.011	Q.158 O	Wheat milled by-products	Y

CA 6.4.4 Roultry

A pothery feeding study with parent ethephon was submitted in the Annex II dossier of 2002. The study included three dose groups (1%, 3X and 10X) with a 1X level of 2.3 mg/kg DM, which corresponds to 5.7 and 12 times the maximum estimated exposure in the diet of layer and broiler poultry, respectively. The animals (10 per dose group, distributed in 3 subgroups of 3-4 individuals) were dosed for 28 consecutive days. An overview of the study results is given in Table 6.4.1-1. The active substance was found to be only minimally transferred to tissues and eggs. The residues in eggs were especially low with a maximum of 0.0036 mg/kg in the eggs of the 10X dose group. At the 1X dose rate the highest residues of ethephon were < 0.010 mg/kg in muscle, 0.014 mg/kg in fat and skin and 0.033 mg/kg in liver.

The potential residues of parent ethephon in poultry tissues and eggs may be estimated taking into account the potential residues in the feed of poultry and the transfer factors of the poultry feeding study. As shown in Table 6.4.1-1 the anticipated maximum residues of parent ethephon in poultry



tissues and eggs are extremely low (< 0.01 mg/kg). Therefore, based on the representative uses it would be justified to set the MRL of ethephon at 0.01 mg/kg (LOQ) in poultry muscle, fat, liver and eggs.

Table 6.4.1- 1: Overview of hen feeding study results and estimated residues in poultry tissues and eggs

	Re	esults o	f hen feeding st	udy	Estimates based on the tary exposure of poultry for representative uses *				
Commodity	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residive (mg/kg) 《	Nighest O Yesidue (mg/kg)	MR/L proposal (mg/kg)		
	2.3	2	< 0.010	< 0.010					
Muscle	6.9	3	0.012	0.015	0-0013 ©	0,0018	0.01		
	23.0	3	0.037	0.060			0.01 V		
Claire aniels	2.3	2	0.013	QQ14 J		ľ. Oď Š			
Skin with fat	6.9	3	0.024	0.032	100 0017	0.0025	0.01		
	23.0	3	0.093	0.1					
	2.3	2	0.031	0.033					
Liver	6.9	3	0.062		05040	0.0058	0.01		
	23.0	3	0.237	0.289					
	2.3	3	₹0.002	< 002 × 1	Q h				
Eggs	6.9	3	< 0.000	≤ 0.002°>	0.0003	0.0004	0.01		
	23.0	Ø,	0.003	0.004					

^{*} The median and highest residues in poultry tissues and eggs were estimated based on the maximum transfer factors of the hen feeding study for the mean and maximum residues, respectively. The maximum transfer factors were always found at the 1X dose level (2.3 rw/kg DM). The maximum and median dietary exposures used for the calculation were 0.403 mg/kg DM and 0.298 mg/kg DM, respectively.

CA 6.4.2 Ruminants

A cow feeding study with parent ethephon was stomitted in the Annex II dossier of 2002. The study included three dose groups (1X, 3X and 10X) with a 1X level of 43 mg/kg DM, which corresponds to 31 times the maximum estimated exposure in the diet of dairy cattle. The animals (3 per dose group) were dosed for 28 consecutive days. An averview of the study results is given in Table 6.4.2-1. Ethephon was only slightly transferred to milk and edible tissues. At the 1X dose level, the highest residues of ethephon were 0.007 mg/kg in milk, < 0.01 mg/kg in fat, 0.016 mg/kg in muscle, 0.095 mg/kg in liver and 0.00 mg/kg in kidney.

The potential residues of parent ethephon in cattle tissues and milk may be estimated taking into account the potential residues in the feed of beef and dairy cattle and the transfer factors of the cow feeding study. As shown in Table 6.4.2-1, the residues of parent ethephon may reach 0.038 mg/kg in cattle kidney and arcanticipated to remain < 0.01 mg/kg in cattle muscle, fat, liver and milk. Therefore, based on the representative uses it would be justified to set the MRL of ethephon at 0.04 mg/kg in cattle kidney and 0.01 mg/kg (LOQ) in cattle muscle, fat, liver and milk. The results of cow feeding study may also be used to estimate the potential residues of ethephon in sheep tissues and milk. The calculation details are shown in Table 6.4.2-2. Using this approach and based on the representative uses, it would be justified to set the MRL of ethephon at 0.02 mg/kg in sheep liver, 0.07 mg/kg in sheep kidney and 0.01 mg/kg (LOQ) in sheep muscle, fat and milk.

Table 6.4.2-1: Overview of cow feeding study results and estimated residues in cattle tissues and milk

	Re	sults o	f cow feeding st	tudy	Estimates based on dietary exposure of cows for representative uses*				
Commodity	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest Sesidue (mg/kga/	MRL proposal eng/kg		
	43	3	0.013	0.016			A		
Muscle	129	3	0.051	0.061	0,0002	0.0007	0.01		
	430	3	0.117	0.170					
	43	3	< 0.010	< 0.010					
Fat	129	3	0.041	0.069	0-0001	0.0007	0.01		
	430	3	0.065	0.127		8			
	43	3	0.082	0,095 🞾	0.0017		S.		
Liver	129	3	0.511	€646 Q	0 20017	0.0070	0.01		
	430	3	0.994	1.503(
	43	3	0.486	0.638					
Kidney	129	3	3.177	ð:509 👸	0.0103	0.0378	0.04		
	430	3	7.846	10.918					
	43	3	19.907 Ç	0.007		Y			
Milk	129	3€	0.16	Q 019 💥	0,0005	0.0002	0.01		
	430		0.03Q	0.033					

The median and highest esidues in cattle issues and milk were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found withe 3X dose level (129 mg/kg DNQ, exceptor the highest residues in milk, for which the maximum transfer factor was obtained at the 1X dose level 43 mg/kg DM). Especially for liver and kidney, the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered suitable to estimate the dose levels far below the 1X level of the study. The maximum and median dretary exposures used for the calculation were 1.391 mg/kg DM and 0.417 mg/kg DM, respectively. a non-negligible ordinate at the origin and therefore, were not considered suitable to estimate the residues at

Table 6.4.2- 2: Overview of cow feeding study results and estimated residues in sheep tissues and milk

	Re	sults o	f cow feeding st	tudy	Estimates based on dietary exposure of sheep for representative uses*				
Commodity	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest Sesidue (mg/kga/	MRL proposal (mg/kg)		
	43	3	0.013	0.016			A		
Muscle	129	3	0.051	0.061	0,0002	0.001/2	0.01		
	430	3	0.117	0.170					
	43	3	< 0.010	< 0.010					
Fat	129	3	0.041	0.069	0.0002	0.000	0.01		
-	430	3	0.065	0.127		8			
	43	3	0.082	0,095 💖	0.0025		Ç		
Liver	129	3	0.511	0.646 Q	0 0025	0.0129	0.02		
	430	3	0.994	1.503(
	43	3	0.486	0.638					
Kidney	129	3	3.177,0	ð:309 🖔	0.0154	0.0700	0.07		
	430	3	7.846	10.918					
_	43	3	10,007	0.007	Ø. 1	A			
Milk	129	3	0.16	Q019 💥	0,0008	0.0004	0.01		
	430		0.030	0.033					

^{*} The median and highest residues in sheep vissues and milk were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found at the 3X dose level (129 mg/kg DNQ), except or the highest residues in milk, for which the maximum transfer factor was obtained at the 1X dose level (43 mg/kg DM). Especially for liver and kidney, the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered suitable to estimate the residues at dose levels far below the 1X tovel of the study.

The maximum and median detary exposures used for the calculation were 2.572 mg/kg DM and 0.624 mg/kg DM, respectively.

CA 6.4.3 Pigs

The potential residues of parent ethephon in pig tissues may be estimated taking into account the potential residues in the read of breeding and finishing swine and the transfer factors of the cow feeding study.

Based on the outcome of the calculation (Table 6.4.3-1) and considering the herein supported representative uses it would be justified to set the MRL of ethephon at 0.01 mg/kg (LOQ) in pig muscle, fat, liver and kidney.

Table 6.4.3-1: Overview of cow feeding study results and estimated residues in pig tissues

	Re	sults o	f cow feeding st	tudy	Estimates based on dietary exposure of cows for representative uses*			
Commodity	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest residue (mg/kg)	MRL proposal (14g/kg)	
	43	3	0.013	0.016				
Muscle	129	3	0.051	0.061	0,0001	0.0001	0:01	
	430	3	0.117	0.170				
	43	3	< 0.010	< 0.010	Y , O (
Fat	129	3	0.041	0.069	0.0001	0.0001	Ø.01 °	
	430	3	0.065	0.127		ک (س) ک		
	43	3	0.082	0.09\$\bigg\forall^{\gamma}				
Liver	129	3	0.511	0:646	0.00	0.00126	Q Q .01	
	430	3	0.994	∑503 ♀		\$ 6°	٥	
	43	3	0.486	0.638		V W		
Kidney	129	3	3.177	3,509	0.000	0.0072	0.01	
	430	3	7.846	O0.918 👰				

^{*} The median and highest residues in pig tissues were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found at the 3X dose level (129 mg/kg M). Expecially for liver and kidney the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered outable to estimate the residues at dose levels far below the 1X level of the study.

The maximum and median dietary exposures used for the calculation were both 0.267 mg/kg DM.

CA 6.4.4 Fish

No suitable test method for fish feeding studies is listed in Commission Communication 2013/C 95/01 about the implementation of regulation (EU) No 283/2013. Therefore, this point does not need to be addressed.

However, according to the working document SANCO/11187/2013 rev. 3 on the nature of pesticide residues in fish it seems that in future the nature and magnitude of residues in fish only need to be investigated for active substances that are fat soluble, i. e. substances with log Pow \geq 3. Since ethephon is hydrophric (log Pow \rightarrow 1.89 at \rightarrow H 7), it is expected that even when a suitable test method has been assued no fish feeding study will be required for ethephon.

CA 6.5 Effects of processing

CA 6.5.1 Nature of the residue

A model hydrolysis rudy with [U-14C]-ethephon to investigate the nature of the ethephon-derived residues in processed commodities is included in the Annex II dossier of 2002 and was reviewed in the Draft Assessment Report issued by the Rapporteur Member State in 2004. Ethephon was shown to hydrolyze to ethylene as the main degradation product. The degradation rate differed significantly depending on the tested conditions. While under conditions representative of pasteurization (pH 4, 90°C) about 10% of the active substance was degraded to ethylene, more than 75% was degraded to ethylene under conditions representative of brewing, baking, boiling, or sterilization (pH 5, 100°C; or



pH 6, 120°C). The thus formed ethylene was entirely released into the atmosphere. Minor degradation routes resulted in the formation of HEPA and an unknown product, which totalled less than 10% of the initial amount of ethephon.

Based on these results the residue definition in the processed commodities was considered to be parent ethephon, like in the raw agricultural commodities (EFSA Reasoned opinion on the review of the existing MRLs for ethephon, EFSA Journal 2009;7(10):1347).

CA 6.5.2 Distribution of the residue in peel and pulp

Studies to investigate the distribution of residues in peel and purp are not relevant to coeals. Therefore, no data on the distribution of residues between peel and purp need to be submitted for the herein supported representative uses.

CA 6.5.3 Magnitude of residues in processed commodities

Information about the residues of ethephon in processed careal commodities was arready provided in the Annex II dossier of 2002. However, in the then submitted studies the samples of grain and grain processed commodities were extracted with methanol, which is not in line with the extraction procedure of the wheat metabolism study. In order to comply with new data requirements [Regulation (EU) No 283/2013) and new guidelines [OECD Condance document on perficide residue analytical methods, ENV/JM/MONO(2007)17] it was decided to conduct new processing studies, in which the samples were extracted in the same way as in the wheat metabolism study (i.e. First by blending with methanol and then by digestion with hydrochronic acid).

- Processing of wheat

Report: K. A 6.5.3 (20)5; M-533330-02-7

Title: Determination of the residues of ether phon in wheat, soft and the processed

fractions (semotina; brant middlings; semotina bran; shorts; white flour; whole meal; whole meal bread; when germ; starch A gluten; starch B and gluten feed meal) after

spraying of thephon SL 480 or the field in Germany

Report No.: \$\square\$ 13-3406

Document No. 7 - M-532330-02-

Guideline(s): Regulation (Et No 11/07/2009 of the European Parliament and of the Council of 21

October 2009 concerning the placing of plant protection products on the market and repealing Souncil Directives 79/117/EEC and 91/414/EEC,

EC Guidance working document 7029/VI/95 rev.5 (1997-07-22).

OECD 509 Adorted 2009-09-07, OECD Guideline for the Testing of Chemicals, Crop

Field Trial

OECD 50%, Adopted 2008-10-3, OECD Guideline for the Testing of Chemicals,

Magnitude of Pesticide Residues in Processed Commodities

QUS EPAOCSPR Guideline No. 860.1500

Guideline deviation(s): none GLP/GEP: ves

Materials and methods

A field trial was conducted in Germany during the 2013 growing season in order to obtain ethephon-treated wheat grain for a processing study. The product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the rate of 720 g as/ha after dilution in 300 L/ha of water. Wheat grain was harvested at



maturity (BBCH 89), which was 75 days after application. The harvest was divided in three types of field samples :

- A sample of ≥ 1 kg that was deep frozen on the day of harvest and kept at ≤ -18°C until analysis.
 The purpose of this sample was to determine the residues in the raw agricultural commodity on the day of harvest.
- A field sample of about 50 kg intended for processing, which was kept at applient temperature until the beginning of processing.
- Two field samples of ≥ 1 kg that were stored under the same conditions as the samples for processing and deep frozen at the beginning of processing. The purpose of these samples was to determine the residues in the raw agricultural commodity at the beginning of processing.

Details about the design and results of the field trial are given in Take 6.5 3 21.

Table 6.5.3- 1: Field trial conducted to generate wheat grain for processing overview of trul design and residue results [Study 13-3406]

Report	Location	Forn	nulation	,	ĄĮ	plicati	on A	Cran	Reddues of	DALT
Study Trial	Country Year	Туре	Content	No k	g as ha	kg as/ hLQ	Growth stage	Cropi part	thephon (mg/kg)	(days)
M-533330-02-1 13-3406 13-3406-01	2013	SL	480		¥.72	9 ,24	BBCH 51	grain	0.077*	75

DALT: days after last treatment

The raw agricultural commodity for the processing phase was shipped to the processing site 2 days after harvest and stored at arbient temperature until the beginning of processing, which was 105 days after harvest. The 50 kg field sample was divided to four subsamples for the various processes to be investigated during the study:

- A subsample of ca 40 kg for the preparation of semelina and white flour.
- A subsample of car. 10 kg for the preparation of wholemeal flour and wholemeal bread.
- A subsample of ca. 20 by for the preparation of wheat germs.
- A subsample of ca. 10 kg for the preparation of starch and gluten.

Each subsample was first cleaned to remove foreign matters and impurities. Thereafter the cleaned grain was conditioned by slightly increasing the moisture content from 14.8% to 15.2%.

Milling was performed by using a roller mill. In this type of device, grain is crushed by passing between pairs of rollers. As the grain material progresses through the machine the spacing between the rollers decreases, which yields milled commodities of decreasing particle size. At each step of the milling process, sifters allow separation of different types of milled commodities.

Semonia and semolina bran were produced at the very beginning of the milling process. By further milling and severing, straight flour was obtained from semolina while coarse bran and fine bran (middlings) were obtained from semolina bran. The bran fractions were combined again and centrifuged to wild low-grade meal and shorts. White flour (type 550) was obtained by mixing straight flour and low-grade flour in appropriate amounts to reach a mineral content of 0.51-0.63%.

For wholemeal flour production, the combined coarse bran and fine bran fractions were ground to produce low-grade meal and fine shorts. The straight flour, low-grade flour and fine shorts were mixed to obtain wholemeal flour. Wholemeal bread (1.6 kg) was prepared with wholemeal flour (1.3 kg), yeast (52 g), salt (26 g) and water (0.91 L) which were mixed, kneaded, let stand for fermentation and baked at 210°C for 50 minutes.

^{*} Residue level measured in the sample frozen on the day of harvest.



For the preparation of wheat germ the grain was broken by passing successively between pairs of rollers with a decreasing spacing (0.5, 0.3 and 0.2 mm). The fraction with a particle size of $400-1000~\mu m$ was collected by sieving. Coarse bran was removed by gravity separation. The remaining fraction consisting of middlings and germs was further milled and sieved to obtain flour, bran and germs.

For the preparation of starch and gluten the straight flour (1 kg) was mixed with water (1.2 L). The thus obtained dough was centrifuged to separate process water, wet starch and gluten. The process was repeated twice with the starch fraction. The thus obtained starch was dried ab 60°C to produce "starch A". The gluten fractions of the previous steps (which also contained some starch) were washed repeatedly and centrifuged with the process water in order to separate (purified) gluten, (remaining) starch and fibre. Starch was dried at 60°C to produce starch B. Fibre was also dried at 60°C while gluten was dried by freeze drying. The dried commodities were milled. Gluten feed meal was obtained by mixing starch B, dried gluten and dried fibre.

Representative samples of the <u>underlined</u> processing fractions were taken for analysis and deep frozen at < -18°C within less than 24 hours of sampling

Simplified flow charts of the various processes are shown in Figure 6.5.3-1 Preparation of semolina and white flour), Figure 6.5.3-2 (Preparation of wholemed flour and wholemeal bread), Figure 6.5.3-3 (Preparation of germs) and Figure 6.5.3-4 (Preparation of starch and gotten).

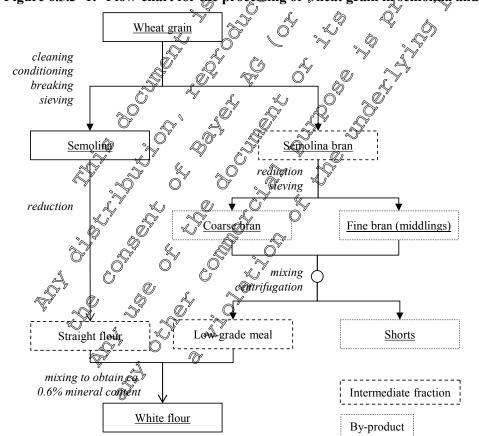


Figure 6.5.3-1: Flow-chart for the processing of wheat grain in semolina and white flour

Analysed fractions underlined

Figure 6.5.3- 2: Flow-chart for the processing of wheat grain in wholemeal flour and wholemeal bread

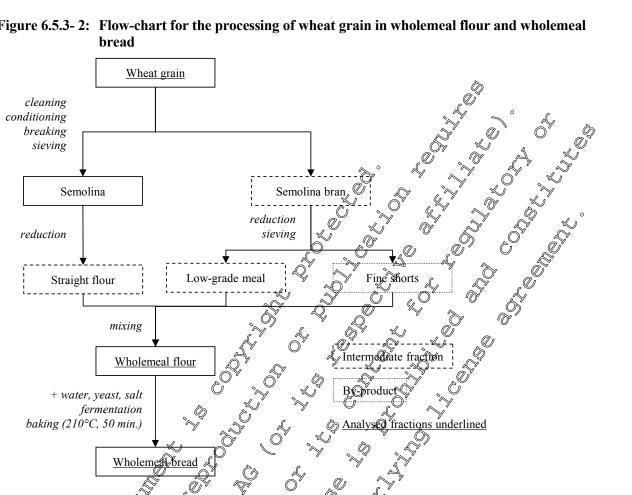


Figure 6.5.3- 3: Flow chart for the processing of wheat grain in wheat germ

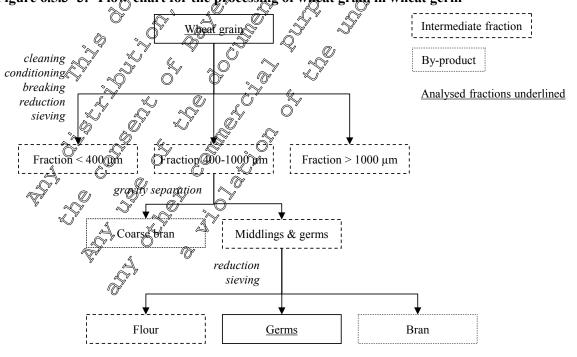
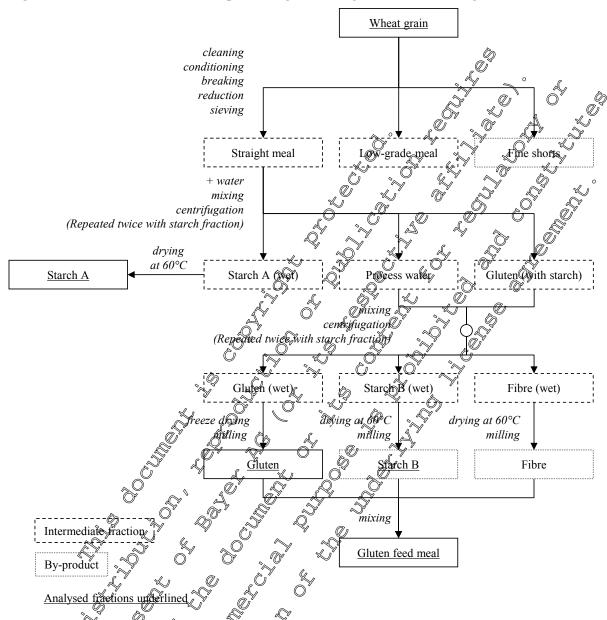


Figure 6.5.3- 4: Flow-chart for the processing of wheat grain in starch and gluten



The unprocessed wheat grain and the various processed wheat commodities were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 30°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by KC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain. In the context of the study 3-3406 limited validation sets (3 replicates at each 0.01 mg/kg and 0.1 mg/kg) were run to demonstrate the applicability of the method for the determination of ethephon in semolina, middlings, wholemeal bread, gluten and starch. These validation data were considered to also cover the residue determination in comparable processed commodities (bran, germs, shorts, white flour, wholemeal flour, gluten meal feed).



The unprocessed grain samples which were frozen immediately after sampling in the field were stored deep-frozen for a maximum of 667 days (less than 23 months) before analysis. The samples taken during processing (including the wheat grain samples taken just before the beginning of processing) were stored deep-frozen for a maximum of 574 days (less than 20 months) before analysis.

Findings

The method validation data and procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3-2. Based on these results the limit of quantification of the method 01429 for the determination of parent ethephon residues in wheat processed commodities was established at 0.01 mg/kg.

Table 6.5.3- 2: Validation data and concurrent recoveries for the determination of parent ethephon residues in wheat grain and wheat processed commodities [Study 13-3406]

			* . O		<i>(7)</i>	
Report (Method)	Matrix	Fortification level [mg/kg]	replicates		Mean [%]	RSD [%]
M-533330-02-1 (01429)	Wheat grain	01.0 voverall	2 4	97-98 5 97-98 5 \$9,95 7 5 -	98 92 95	- 4.3
M-533330-02-1 (01429)	Wheat semolina	001 0.10 0.10 0 1.0 0 overall		88, 96, 98 Q, 96, 97, 98 Q, 93 P, 29 -	92 97 93 94	5.8 1.0 - 4.3
M-533330-02-1 (01429)	Where middlings	0.10 1.0 vergat		95, 96, 100 95, 98, 103 95	97 99 95 97	2.7 4.1 - 3.2
M-533330-02-14 (01429)	Whotemeal Wheat bread	001 0.10 overall	3 3 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	79, 83, 89 85, 92, 94 -	84 90 87	6.0 5.2 6.5
M-533330-02-1 (01429)	Wheat germ	001 010 Everall	3 2 5	90, 97, 105 80, 88 -	97 84 92	7.7 - 10.3
M-533330-02-1	Wheat gluten	0.01 0(1)0 @erall	3 3 6	104, 107, 112 89, 101, 105	108 98 103	3.8 8.5 7.5
M-533330-02-1 (01429)	Wheat starch	0.01 0.10 overall	3 3 6	77, 89, 97 93, 95, 97 -	88 95 91	11.5 2.1 8.4

The fortification levels are expressed as ethephon.

The residues of parent ethephon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.3-3. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain (semolina bran, bran, middlings, shorts and germs) while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. Comparison between the residue



levels in wholemeal and wholemeal bread indicates that about 66% of the ethephon residues degraded during baking.

Table 6.5.3- 3: Residue levels and transfer factors for parent ethephon in wheat processed commodities [Study 13-3406]

		· ~ · · · ·
Processing type	Trial 13-3406	(Germany)
Processed commodity	Residues (mg/kg)	Frocessing factor
Raw agricultural commodity		
Wheat grain	\$0.070*\$\tag{\text{\$\sigma}}\$\text{\$\sigma}\$\$	Processing factor
Preparation of semolina and white flour		3.2 F
Semolina	0.22	(V) (D).52 (V)
Semolina bran	0.26	1
Coarse bran Middlings Shorts White flour	0.40	
Middlings	0.12	T. T
Shorts		2 4.3
Coarse bran Middlings Shorts White flour Preparation of wholemeal and wholemeal bread Wholemeal flour Wholemeal bread Preparation of wheat germ Germs Preparation of starch and dluten		0.19
Preparation of wholemeal and wholemeal bread		
Wholemeal flour		0.99
Wholemeal bread	0.069	0.27
Preparation of wheat germ		
Germs S S	0.17 V	2.4
Preparation of starch and gluten	© 0.17 V	
Starch A O S	\$0.01	< 0.14
Gluten Q Q S	0.01	0.14
Starch B	0.01	< 0.14
Germs Preparation of starch and gluten Starch A Gluten Starch B Gluten feed meal	< 0.01	< 0.14

^{*} Average of the residue oneasured in the two replicate samples frozen at the beginning of processing (0.064 mg/kg/and 0.00 mg/kg/

Conclusion

A trial was performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. The processing factors were 3.7 for bran, 2.4 for germs, 0.52 for semolina, 0.19 for white flour, 0.99 for wholemeal flour and 0.27 for wholemeal bread. The data indicate that ethephon partially degrades during baking. The residues in starch and gluten were $\leq 0.01 \text{ mg/kg (LOQ)}$ with processing factors ≤ 0.14 .



Report: KCA 6.5.3/14; ; ; ; 2015; M-535996-01-1

Title: Determination of the residues of ethephon in/on winter wheat and the processed

fractions (bran; gluten; gluten feed meal; grain, stored; middlings; semolina; semolina

bran; shorts;

starch A; starch B; wheat germ; white flour; whole meal and woolemeal bread) after

spray application of ethephon SL 480 in Germany

Report No.: 14-3401 Document No.: M-535996-01-1

Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of

October 2009 concerning the placing of plant protection products on the market and

repealing Council Directives 79/117/EEC and 91/414/EEC, FEC Guidance working document 7029/N4/95 rev (1997-47-22)

OECD Guideline for the Testing of Chemicals Crop Rield Trial (FG 509 published

September 2009)

OECD 508, Adopted 2008-10-03 OECD Quideline for the Toxting of Chemical's

Magnitude of Pesticide Residues in Processed Commodities US EPA OCSPP Guideline No. 860.1500 on Grop Field Trial

US EPA OCSPP Guideling No. 860 520

Guideline deviation(s): not specified

GLP/GEP: yes

The wheat processing study 13-3406 (see above) was initially designed to include two trials. However, one of these trials had to be cancelled due to crop fature. Therefore a second wheat processing study (14-3401) was initiated in 2014 to generate data from a second trial. Since the study 14-3401 was designed in the same way as the study 13-3406, the experimental approach is not described again in full detail and reference is largely made to the study 33-3406.

Materials and methods

A field trial was conducted in Germany during the 2014 growing season in order to obtain ethephon-treated wheat grain for a processing study. The product Ethepton SL 480 g/L was applied once as a broadcast foliar spray at the rate of \$20 g as a after dilution in 300 L/ha of water. The treatment was intended to be conducted at the growth stage BBCH 51 but had to be conducted at the growth stage BBCH 58 due the late issuance of the study protocol. Wheat grain was harvested at maturity (BBCH 89) which was 66 days after application. The harvest was divided in three types of field samples:

- A sample of hkg that was deep frozen on the day of harvest. The purpose of this sample was to determine the residues in the raw aggicultural commodity on the day of harvest.
- A field sample of about 50 kg intended for processing, which was kept at ambient temperature until the beginning of processing.
- Two field samples of ≥ 1 kg that were stored under the same conditions as the samples for
 processing and deep frozen at the beginning of processing. The purpose of these samples was to
 determine the residues in the raw agricultural commodity at the beginning of processing.

Details about the design and results of the field trial are given in Table 6.5.3-4.

Table 6.5.3- 4: Field trial conducted to generate wheat grain for processing – overview of trial design and residue results [Study 14-3401]

Report Location		Formulation		Application			on	Crdio	Residues of	DALT
Study Trial	Country Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage	Crop part	ethephon o (mg/kg)	(days)
M-535996-01-1 14-3401 14-3401-01	2014	SL	480	1	0.72	0.24	BBCH 58		09.0 \$\frac{1}{2}\frac	66

DALT: days after last treatment

The raw agricultural commodity for the processing phase was supped to the processing site on the day following harvest and stored there at ambient temperature until the beginning of processing, which was 30 days after harvest. The 50 kg field sample of wheat grain was divided in four smaller subsamples which were used for the four following processing types: preparation of semolina and white flour, preparation of wholemeal flour and wholemeal bread, preparation of germs preparation of starch and gluten. Processing was conducted in the same way as in the study \$\overline{93}\$-3406. However, there was no need to condition the wheat grain after cleaning since us moisture content (15%) was already appropriate for milling. Details about the processing operations including simplified flowcharts may be found in the above simmars for the study \$\overline{93}\$-3406. Representative samples of the main processing fractions were taken for analysis and deep fozen at \$\overline{93}\$-18°C within less than 24 hours of sampling.

The unprocessed wheat grain and the various processed wheat commodities were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophnic Interaction 1 quid Chromatography mode. During method validation the limit of quantification (LOO) for exception was established at 0.01 mg/kg in/on cereal grain. In the context of the study 13-3406 (see above) the applicability of the method was also demonstrated for the determination of 0.00 mg/kg. These validation data were considered to also cover the residue determination in comparable processed commodities (bran, germs, shorts, white flour, wholemeal flour, gluten meal feed).

The unprocessed grain samples which were tozen immediately after sampling in the field were stored frozen for 374 days (less than 13 months) before analysis. The samples taken during processing (including the wheat grain samples taken just before the beginning of processing) were stored frozen for a maximum of 356 days (less than 2 months) before analysis. Due to a technical failure, the storage temperature of the taborators samples exceeded -18°C for about 15 hours with a maximum temperature of -12°C. When the samples were transferred in a different freezer they appeared to be still frozen. However, a specific storage stability study (P642151808) was initiated to evaluate the impact of this incident (refer to Point CA 6.1). No significant degradation of ethephon was observed in cereal grain, stars and wholemeal bread after storage at \geq -1°C for 24 hours. It may be concluded that the temperature deviation that occurred during the study 14-3401 had no negative impact on the study results.

^{*} Residue level measured in the sample frozen on the day of harvest

Findings

The procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3-5.

Table 6.5.3- 5: Validation data and concurrent recoveries for the determination of parent ethephon residues in wheat grain and wheat processed commodities [Study 14-3401]

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates	Individual recoveries	Mean recovery	RSD [%]
M-535996-01-1 (01429)	Wheat grain	0.01 0.10 5.0 overall		93,94 0 102 92,93 4	94 102 93 95	- 4.3
M-535996-01-1 (01429)	Wheat semolina	0.01 5.0 overall		79 79 79 79 79 79 79 79 79 79 79 79 79 7	98 79 91	- 12.0
M-535996-01-1 (01429)	Wheat bran	0.01 0.10 0 overally		\$\frac{1}{2}\frac{1}{2	99 98 99	1 1 1
M-535996-01-1 (01429)	Wheat middlings	001 1.0 0 overal		101	101 96 99	
M-535996-01-1 (01429)	Whole nead wheat bread	000 V.0 Coverall		92 98 -	92 98 95	1 1 1
M-535996-01-1 (01429)	WheatQuten	0.000 Oyerall		102 86 -	102 86 94	1 1 1
M-535996-01-1 (01429)	Wheat starch	0.01 1.07 overall		105 94 -	105 94 100	- - -
M-535996-01 (01429)	Wheat gluten	0.01 1,00 overall	1 1 2	108 91 -	108 91 100	- - -

The forturation levels are expressed as etherhon.

The residues of parent etherhon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.306. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain (semolina bran, bran, middlings, shorts and germs) while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. Comparison between the residue levels in wholemeal and wholemeal bread indicates that about 59% of the ethephon residues degraded during baking.

Table 6.5.3- 6: Residue levels and transfer factors for parent ethephon in wheat processed commodities [Study 14-3401]

Processing type	Trial 14-3401	-01 (Germany)
Processed commodity	Residues (mg/kg)	Processing factor
Raw agricultural commodity	4	
Wheat grain	0.27*	
Preparation of semolina and white flour	0.18 5 4 6 6 7 6 7 6 7 6 7 6 7 6 7 6 7 6 7 6 7	0.682
Semolina	×0.18 × 4	
Semolina bran	0.18 0.06 0.65 0.55 0.55 0.55 0.55 0.55 0.55 0.55	25 25 2.5 2.1 5 2.0
Coarse bran	0.55	2.5
Middlings		1) / <u>S.</u> 7 1 @ S
Shorts	0.55	20
Shorts White flour Preparation of wholemeal and wholemeal bread Wholemeal flour Wholemeal bread	Q 2666	⊘ ⊘ 0.25
Preparation of wholemeal and wholemeal bread		
Wholemeal flour	0.20	0.74
Wholemeal bread	0.20	0.74 0.24
Preparation of wheat germ		
Germs	0.41	1.6
Preparation of starch and gluter		
Starch A	< 0.0↑ × × × × × × × × × × × × × × × × × × ×	< 0.04
Gluten	0.00%	0.11
Starch B	9 .012	0.05
Wholemeal flour Wholemeal bread Preparation of wheat germ Germs Preparation of starch and glutent Starch A Gluten Starch B Gluten feed meal	0.014	0.05

^{*} Average of the residues measured in the two replicate samples frozen at the beginning of processing (0.26 mg/kg and 0.27 mg/kg)

Conclusion

A trial was performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain while in the commodities that correspond to the oner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. The processing factors were 2.5 for bran, 1.6 for germs, 0.68 for semolina, 0.25 for white flour, 0.74 for wholemeal flour and 0.24 for wholemeal bread. The data indicate that ethephon partially degrades during baking. The residues in starch and gluten were low with processing factors ≤ 0.05 for starch and a processing factor of 0.11 for gluten.

General conclusion on the processing of wheat

Two trials were performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A comparison of the processing factors obtained during these trials is provided in Table 6.5.3-7. The processing factors from the two trials were found to be comparable according to the criterion of the OECD guideline 508 on the magnitude



of the pesticide residues in processed commodities (difference of less than 50%), except for shorts (difference of 53%). Since shorts are not a major wheat processed commodity and since the difference between the two processing factors is only marginally above 50%, it is not considered necessary to conduct a further wheat processing trial. The residues were found to concentrate in the processed commodities which correspond to the outer parts of the grain (median processing factors of 3.1 for bran, 3.2 for shorts and 2.0 for germs) while in the commodities that correspond to the inner parts of the grain the residues were less than in whole grain (median processing factors of 0.60 for schooling) 0.22 for white flour, 0.87 for wholemeal flour and about 0.1 for gluten and parch)

Table 6.5.3-7: Compilation of processing factors for ether on in wheat processed commodities

Processing type		Processin	g factors S	
Processed commodity	Trial 13-3406-01 (Germany)	Trial 44-340/501	Difference *	Median
Preparation of semolina and white flour	4			
Semolina	0.52	Q 0.680	24%	0.60
Semolina bran	3.2		J 27%	2.9
Coarse bran	207	2.5	32%	3.1
Middlings	(1.7) (1.7) (1.3) (1.3) (1.3)	2.1	19%	1.9
Shorts	\$ 4.3°	2.6	53%	3.2
White flour		0.25 Q	5 24%	0.22
Preparation of wholemeal and wholemeal bread Wholemeal flour				
Wholemeal flour	0.99	9 .74	25%	0.87
Wholemeal bread	Ø.27 F	0.24	11%	0.26
Preparation of wheat germ		<i>3 3</i>		
Germs		©1.6	33%	2.0
Preparation of starch and gluten	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	W.		
Starch A Gluten Starch B		< 0.04	n.a.	< 0.09
Gluten		0.11	21%	0.13
Starch B	0.140	0.05	n. a.	< 0.10
Gluten feet meal	~ 0 %4	0.05	n.a.	< 0.10

Calculated according to the formula provided in the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities: [Pf (high value) - Pf (low value)]/Pf (high value).

n. a.: Not applicable; the difference between the two processing factors cannot be calculated since at least one of them is not known precisely.





- Processing of barley

; 2016; M-535989-02-1 Report: KCA 6.5.3/15;

Amendment no. 1 to final report no.: 14-3400 - Determination of the residues of Title:

> ethephon in/on spring barley and the processed fractions (beet, grain, stored; hops draff; malt sprouts; brewers yeast; brewers malt; brewers grain; pearl barley and pearl barley rub off) after spray application of ethephon SL 480 in Germany and the

Netherlands

Report No.: 14-3400 Document No.: M-535989-02-1

Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 Guideline(s):

October 2009 concerning the placing of plant protection products on the market and

repealing Council Directives 79/11 FEEC and 91/41 FEC, EC Guidance working document 029/VL rev.5 (1997-07-22),

OECD Guideline for the Testing of Chemicals, Grop Field Trial (TG 509 politished

September 2009)

OECD 508, Adopted 2008-10-03, OECD Guirdeline for the Testing of Chemicals,

Magnitude of Pesticide Residues in Processed Commodities US EPA OCSPP Guideline No. 860.15000 Crop Field Tigal

US EPA OCSPP Guideline No. 860.1520

Guideline deviation(s): see Appendix 8

GLP/GEP: yes

Materials and methods

Two field trials were conducted in Germany and the Netherlands during the 2014 growing season in order to obtain ethephon-treated backey grain for a processing study. In each trial the product Ethephon SL 480 g/L was applied once as a broad ast follow spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the rate of 720 g as/ha after dilution in 300 L/ha of water. Barley grain was harvested at matority, worch was 49 and 38 days after application in the two trials, respectively. In each trial the harvest was divided in three types of field samples:

- A sample of 1 kg that was the prozen on the day of harvest. The purpose of this sample was to determine the residues in the raw agricultural commedity on the day of harvest.
- Two field sample of about 25 kg for processing into beer and 5 kg for processing into pearl barley, which were kept at ambient temperature until the beginning of processing.
- Four field samples of 1 kg that were stored ander the same conditions as the samples for processing and deep frozen at the beginning of processing (two samples per processing type). The beginning of processing.

 Details about the design and results of the field trial are given in Table 6.5.3-8. purpose of these samples was to desermine the residues in the raw agricultural commodity at the

Table 6.5.3- 8: Field trials conducted to generate barley grain for processing – overview of trial design and residue results [Study 14-3400]

Report	Location	Formulation			Aj	pplicati	on	Crelio	Residues of	DALT
Study Trial	Country Year	Туре	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage	Crop part	ethephon o (mg/kg)	(days)
M-535989-02-1 14-3400 14-3400-01	2014	SL	480	1	0.72	0.24	BBCH 51	grain, G		Q 49
M-535989-02-1 14-3400 14-3400-02	2014	SL	480	1	0.72	0.24 O	BBCN 51	grain V	2.3*	38

DALT: days after last treatment

Note: In the trial 14-3400-02 the barley was sown at an inusually late (ate (25% pril 2644)). Because of that, the crop developed extremely quickly 38 days between application at BBCH 51 and mature harvest). This probably accounts for the higher residue levels found in this Gal (up to 2.4 mg/kg of parent ethephon in grain). Therefore, the Gal is not considered valid for MRL-setting. Under normal conditions the minimum time between application at BBCH 51 and mature harvest is expected to be about 50 days. The trial, however, is considered valid for the determination of the transfer of ethephon residues in processed barley commodities. According to the DECD guideline 508 on the magnitude of the pesticide residues in processed commodities it is acceptable to shorten the PHI in order to ensure the presence of measurable residues in the raw agricultural commodity.

The raw agricultural commodity for the processing phase was shipped to the processing site 3-6 days after harvest and stored at ambient temperature until the beginning of processing, which was 19-35 days after harvest. The field samples of about 25 kg and 5 kg were used for processing into beer and pearl barley respectively.

The field samples of barley grain were first cleaned in a winnowing machine to remove soil particles and other impurities.

For the preparation of beer, the cleaned barkey grain was first steeped in water at 12-15°C in order to increase the moisture content of the grain to 40-45%. The steeping process consisted of wet steeping phases, during which the grain was soaked in water, and dry steeping phases, during which the soaked grain was ventilated. In total there were three wet steeping phases, which were separated by two dry steeping phases. Thereafter in order to include germination the steeped grain was kept for nearly 6 days at about 1 °C under continuous stirring. The germination phase was stopped by heating the germinated grain stepwise, first at 45-55°C for 15-16 h, then at 60-70°C for 2 h and finally at 80-90°C for 5 h. By this process (known as killo-drying) malt with a moisture content of 4.9-5.0% was obtained. In the next step, the germs were separated mechanically from the malt with a trimmer to produce malt sprouts and brewer's malt.

For brewing the brewer's malt was milled and mixed with water. The resulting mash was heated successively at 55°C, 62°C, 72°C and finally at 76°C. The whole mashing step lasted for about 2 h. The aqueous malt extract (wort) was then separated from the insoluble malt components (brewer's grain). The malt extract remaining on brewer's grain was washed with hot water and combined with the wort. After addition of hop pellets, the wort was boiled for 90 min. at normal pressure and cooled down to 18.5-18.8°C. The flocs (hop draff) where separated by producing a whirlpool which caused the sludge to deposit on the bottom of the vat. The fermentation process was induced by adding yeast and lasted for about 9 days. During this time the wort temperature was maintained at about 9°C. At

^{*} Residue level measured in the sample frozen on the day of harvest



the end of the fermentation process the yeast deposit at the bottom of the tank was sampled as <u>brewer's yeast</u>. For maturation the young beer was first kept at room temperature (20°C) for two days before being stored under pressure at 2°C for 4 weeks. After maturation the final product (<u>beer</u> ready for consumption) was obtained by filtration.

For the preparation of pearl barley, the cleaned barley grain was hulled using a decorticator until an abrasion level of 33% was reached. This resulted in <u>pearl barley</u> and <u>barley</u> and

Representative samples of the <u>underlined</u> processing fractions were taken for analysis and deep trozen at < -18°C within less than 24 hours of sampling.

Simplified flow charts of the two processes are shown in Figure 6.5.3- 5 (Preparation of beer) and Figure 6.5.3- 6 (Preparation of pearl barley).

Figure 6.5.3-5: Flow-chart for the processing of Darley grain in beer

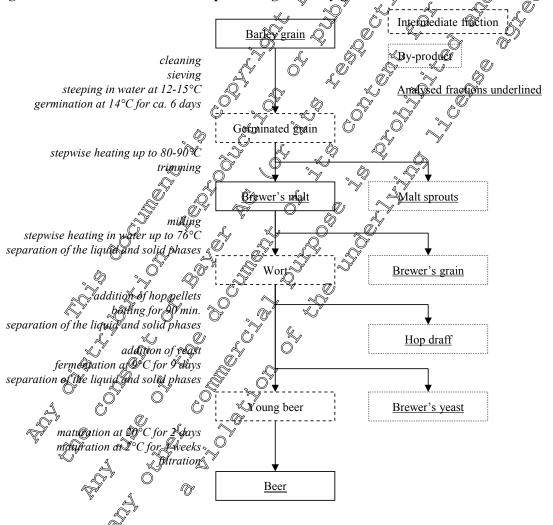
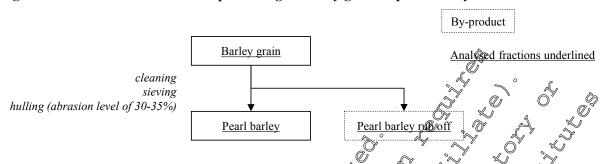


Figure 6.5.3- 6: Flow-chart for the processing of barley grain in pearl barley



The unprocessed barley grain and the various processed barley commodifies were analysed for the residues of parent ethephon according to the method 04429. The residues were extracted from solid samples by blending three times with methanol followed by digestion with a maxture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. For the analysis of beer the residues were extracted by blending once with methanol. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Lund SCX5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction) quid Chromatography) mode During method validation the limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain. In the context of the study 14-3400 fimited validation sets of replicates at each 0.01 mg/kg and 0.1 mg/kg) were run to demonstrate the applicability of the method for the determination of ethephon in malt sprouts, hop draff and pearl barley. These validation data were considered to also cover the residue determination in comparable processed commodities (brewer's grain, brewer's malt, brewer's yeast and pearl barley rub off). Furthermore a complete validation set (5 replicates at each 0.01 mg/kg and 0.1 mg/kg) was run to demonstrate the applicability of the method for the determination of ethephon in beer.

The unprocessed grain samples which were frozen immediately after sampling in the field were stored deep-frozen for a maximum of \$6 days (less than 12 months) before analysis. The samples taken during processing (including the barley grain samples taken just before the beginning of processing) were stored deep-frozen for a maximum of \$32 days (about 1 months) before analysis. Due to a technical failure the storage temperature of the laboratory samples exceeded -18°C for about 15 hours with a maximum temperature of -1.2°C. When the samples were transferred in a different freezer they appeared to be still frozen. However, a specific storage stability study (P642151808) was initiated to evaluate the impact of this incident (refer to Point CA 6.1). No significant degradation of ethephon was observed in cereal grain, malt sprouts and beer after storage at \geq -1°C for 24 hours. It may be concluded that the temperature deviation that occurred during the study 14-3400 had no negative impact on the study results.

Findings

The method calidation data and procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3.8. Based on these results the limit of quantification of the method 01429 for the determination of parent ethephon residues in barley processed commodities was established at 0.01 mg/kg.

Table 6.5.3- 9: Validation data and concurrent recoveries for the determination of parent ethephon residues in barley grain and barley processed commodities [Study 14-3400]

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries	Mean recovery [%]	RSD [%]
M-535989-02-1 (01429)	Barley grain	0.01 0.10 1.0 5.0 overall	2 2 2 1 7	100 54 2 106 92 0 98, 84 7 89 89 89	87 99 91 4 89 4	- 11.7
M-535989-02-1 (01429)	Brewer's malt	0.01 0.10 5.0 overall		99 99 92 4 1	99 99 92 92	- 4.2
M-535989-02-1 (01429)	Malt sprouts	- ~\\\>		95, H2, 105 ° 93, 101, 125 ° 96, ° 9	101 104 96 101	5.1 11.8 - 8.0
M-535989-02-1 (01429)	Brewer's grain	0.01 0.10 50 overall		89 92 0 109 -	89 92 109 97	- - - 11.2
M-535989-02-1 (01429)	Hop draff	0.01 0.10 overall		95, 96 94, 94, 98 -	93 95 94	5.3 2.4 4.0
M-535989-02-1 (01429)	Brewer's yeast	0.01 0.10 5.00 overall		106 99 87 -	106 99 87 97	- - - 9.9
M-535989-02 (01429)	Beer	0.01 0.10 1.0 0 verall	**************************************	91, 92, 96, 97, 103 98, 100, 101, 105, 107 102 -	96 102 102 99	5.0 3.6 - 5.1
M-535989-02-1 (01429)	Pearl bailey	0.01 0.10 5.0 9 yerall	3 3 1 7	103, 103, 107 95, 96, 97 92 -	104 96 92 99	2.2 1.0 - 5.4
M-535989-02-1 (01429)	Pearl barley rub off	0.01 0.10 5.0 overall	1 1 1 3	97 97 92 -	97 97 92 95	- - 3.0

The fortification levels are expressed as ethephon.

The residues of parent ethephon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.3-10. A comparison of the processing factors obtained during these trials is provided in Table 6.5.3-11.

During the malt and beer processing a concentration of the residues was only observed in malt sprouts while in brewer's malt and all the other by-products the residues were less than in the raw agricultural



commodity. Due to dilution with water, the residues were < 0.01 mg/kg (LOQ) in beer. For brewer's malt and malt sprout, the processing factors from the two trials were found to be comparable according to the criterion of the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities (difference of less than 50%). The median processing factors for these commodities were estimated at 0.44 and 1.2, respectively. An accurate comparison of the processing factors for the other commodities of beer processing was not possible since in at least one trial the processing factor could not be calculated.

During the hulling of barley grain a concentration of residues was observed in the processed commodity which corresponds to the outer part of the grain (pearl barley who off) while in the commodity that correspond to the inner parts of the grain (pear) the residues were less than in whole grain. The processing factors from the two trials did not appear to be very consistent, according to the criterion of the OECD guideline 508 (differences of 53-54%). However, on closer examination, the processing factors for the trial 14-3400-01 seem to be overestimated. Based on an abrasion level in barle, is so fresh. I pearl barley is should be at Je. i.e. average residue le this level, the processi. I se respetively Using the s. y and real barley rub off are e. i.e. are extremely consistent (different factor between the residues in pearl b. is proposed to use processing factors of the ectively. These values are conservative since nulling. of 33%, it is expected that pearl barley and pearl barley rub of general 67% and 33% of the raw agricultural commodity, respectively. If no loss of residues occurred during bulling and considering the residues of 0.93 mg/kg and 2.9 mg/kg in pearl barley and pearl varley rub off, respectively, the residues in the raw agricultural commodity showld be at least 0.098 mg/kg (= $67\% \times 0.92 + 33\% \times 10^{-10}$ 2.9), which happens to be the same as the average residue level in the raw agricultural commodity before the beer processing. Based on this level, the processing factors for pool barley and pearl barley rub off are estimated at 0.59 and 1.8, respectively Using Be same approach for the other trial, the processing factors for pearl barley and pearl barley rub of are estimated at 0.60 and 1.8, respectively, which suggests that the two trials are stremely consistent (difference of about %). This is because in both cases there is a 3-fold factor between the residues in pearl barrey rub off and the residues in pearl barley. Therefore, it is proposed to use processing factors of 0.60 and 1.8 for pearl barley and pearl barley rub off, respectively. These values are conservative since it is assumed that there was no



Table 6.5.3- 10: Residue levels and transfer factors for parent ethephon in barley processed commodities [Study 14-3400]

Processing type	Trial 14-3400-	-01 (Germany)	Trial 14-3400-0	2 (Netherlands)
Processed commodity	Residues (mg/kg)	Processing factor	Residues (mg/kg)	Processing o factor
Preparation of beer			Ž ,0	
Barley grain (RAC)	0.098* (0.14, 0.055)	Ö°	© 2.0* © (1.5, 2,4)	
Brewer's malt	0.046	20,4 7	7 <u>(0</u> 78	0,40
Malt sprouts	0.10	1.0	2.7	\$ 1.4 \(\tilde{\chi} \)
Brewer's grain	< 0.01	~ Q.D°	0.04	O 0.0 2 5
Hop draff	< 0.01	0.1	0.073	6 37
Brewer's yeast	< 0.01	\$\frac{1}{2}\tag{0.1}	\$0.070\$°	0.036
Beer	< 0.001	Q < 0 94	< 601	< 0.005
Preparation of pearl barley				
Calculation 1				
Barley grain (RAC)	0,0 Q * (0.057,0.06%		28, (2.4, 2.1)	-
Pearl barley	0.058	© 0.94 Q	0.99	0.44
Pearl barley rub off	018 3	200	3.0	1.3
Calculation 2	0 4		y	
Barley grain (RAC)	0.098		1.65	-
Pearl barley	0.058	0.59	0.99	0.60
Pearl barley rub off	3 .18 3	% .8	3.0	1.8

^{*} Average of the residues measured in the two replicate samples frozen at the beginning of processing. The individual values are shown in brackets

Calculation 1: calculation of processing factors based on the mean residue levels measured in barley grain.

Calculation 2: calculation of processing factors based on the residue levels in barley grain estimated based on the residues in pearly barley and pearly barley barley barley barley and pearly barley barley



Table 6.5.3-11: Compilation of processing factors for ethephon in barley processed commodities

	1							
Processing type	Processing factors							
Processed commodity	Trial 14-3400-01 (Germany)	Trial 14-3400-02 (Netherlands)	Difference	Median				
Preparation of beer								
Brewer's malt	0.47	0.40	\$% \(\tilde{U} \)	0.44				
Malt sprouts	1.0	1.4	26%	1.25				
Brewer's grain	< 0.1	0.02	ma.) ×9.06				
Hop draff	< 0.1	0.037	y yn a.	~ 0.07 ·				
Brewer's yeast	< 0.1	₹9 .036	n. a.S	< 0.07				
Beer	< 0.1	< 0.005	g ng. (29.05				
Preparation of pearl barley	~//			(V				
<u>Calculation 1</u>				Š				
Pearl barley	0.94	0.46 ×	50%	0.69				
Pearl barley rub off	2.5		\$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	2.1				
Calculation 2								
Pearl barley	0.59	0.60		0.60				
Pearl barley rub off		Ø.8 Ø	1%	1.8				

- * Calculated according to the formula provided in the SECD galdeline \$88 on the magnitude of the pesticide residues in provessed commodities: [Pf (high value) Pf Now value)]/Pf (high value).
- n. a.: Not applicable; the deference between the two processing factors cannot be calculated since at least one of them is not known precisely.

Calculation 1: calculation of processing factors based on the mean estimated in barley grain.

Calculation 2: calculation of processing factors based on the residue levels in barley grain estimated based on the residues in pearl barley and pearl barley rule off assuming an abrasion factor of 33% and no loss of residues during hulling.

Conclusion

Two trials were performed to investigate the face of parent ethephon residues during barley grain processing into beer and pearl barley. During the processing in beer a concentration of residues was only observed in that sprout while in all the other processed commodities the residues were less than in barley grain. During the processing integer grain a concentration of residues was observed in pearl barley rub off while the residues in pearl barley were less than in barley grain. The median processing factors were 1.2 for malt sprouts, 0.44 for brewer's malt, 0.60 for pearl barley, 1.8 for pearl barley rub off, < 0.1 in brewer's grain, hop draff and brewer's yeast, and < 0.05 in beer.



CA 6.6 Residues in rotational crops

CA 6.6.1 Metabolism in rotational crops

The confined rotational crop study submitted in the baseline dossier of 2002 was summarised as follows in the EFSA Conclusions [EFSA Scientific Report (2008) 174, 1-65]:

A rotational crop study was submitted with ethephon on radishes, collards and wheat. 14C-ethephon steadily declined in soil. Radioactivity in mature plant samples paralleled of decreased at an even faster rate compared to the soil levels. In plant extracts, no radioactive peaks greater than 0.01 mg/kg were detected. Very low levels of ethephon and 2-hydroxyethol phosphonic acid were detected in certain samples of the crops examined (radishes, collards and wheat). The radioactivity found in plant matrices was attributable to incorporation into all categories of biomolecules. Following application of ethephon according to GAP on cereals no residues are expected in follow uporops.

Since the representative use for the renewal of the active substance approval is the same as the representative use considered during the previous review the above conclusion still applies. In this context it is important to note that the confined rotational crop study was conducted using a sandy loam soil of pH 4.6, which – due to the susceptibility of ethernon to basic hydrolysis constitutes a worst case situation with regard to residues. It is also important to note that the study was conducted at the highly exaggerated rate of 2360 g as/ha, which represents about 4 primes the representative use rate of 480 g as/ha. Since ethephon does not accumulate in soil, there is no need to consider the possible plateau concentration in soil.

CA 6.6.2 Magnitude of residues in rotational crops

Based on the results of the confined rotational crop study, no residues of ethephon or ethephon-derived metabolites are expected to ccur in rotational crops at levels ≥ 0.04 mg/kg after the use of ethephon in cereals according to the herein considered representative GAPs. Therefore no field study to determine the magnitude of residues in rotational crops needed.

CA 6.7 Proposed residue definitions and waximum residue levels

CA 6.7.1 Proposed residue definitions

The residue definition of ethephod in food commodities of plant and animal origin was up-dated in the EFSA Reasoned opinion on the eview of the existing MRLs for ethephon (EFSA Journal 2009;7(10):2347).

Residue definition in commodities of plant origin:

Metabolism of ethephon was divestigated in cereals (wheat) and in fruits and fruiting vegetables (tomato and pineapples) (LPSA, 2008a). Additional information on the fate of ethephon was also available after application to squash, cucumber, apple and cherry trees. These studies indicate that metabolism of ethephon in plants mainly proceeds via conversion to 2-hydroxyethyl phosphonic acid (HEPA) and via decomposition via ethylene, which is released in the atmosphere, and phosphate, which is incorporated in the natural phosphate cycle of the plant. The wheat metabolism study shows that in the edible part (grain) of cereals treated at normal field rates, the metabolite HEPA and ethephon are present at similar levels. In tomatoes, HEPA was found to increase over time but 12 days after treatment, which corresponds to the supported PHI for most fruiting crops, the metabolite was still present at levels four times lower than ethephon (The Netherlands, 2004). Moreover, residues trials on grapes where levels of both ethephon and HEPA were measured were reported by the



Netherlands (2009). After a PHI of 28 days, all trials demonstrated that HEPA was present at levels lower or similar to the parent compound. Considering that HEPA was shown to be of different toxicity than the parent compound (see also section 2), there is no need to include HEPA in the residue definition for risk assessment together with the parent compound but the question could be raised whether a separate risk assessment for HEPA would be necessary. EFSA concludes that a separate risk assessment for HEPA will not be more critical than the risk assessment for ethephon because HEPA is not expected to be present in higher amounts than the parent compound and adverse effects for HEPA are expected to occur at exposure levels 5-10 times higher than for ethephon (see also exciton 2). A separate residue definition for risk assessment of HEPA is therefore not required.

Consequently, the residue definition for enforcement and risk assessment in cereals fruits and fruiting vegetables is defined as ethephon only. Validated analytical methods for inforcement of the proposed residue definition are available (see also section 1.1). These conclusions reflect the views of the RMS (The Netherlands, 2008) and are also in line with the findings of the 1994 JMFR (WHOFFAO, 1995). During the peer review of ethephon (EFSA, 2008a) is was decided to include HEPA in the residue definition for risk assessment but this conclusion is no longer relevant as additional information on the toxicity of HEPA has been considered in the meanting.

It is noted that ethephon is also authorised for use on cotton seed, far which no representative metabolism study is available. In order to extend the proposed residue definition be oilseeds, a representative metabolism study for this proposed of a provisional basis to define the residue for enforcement and risk assessment in cotton seeds as ethephon

Residue definition in commodities of animal origin:

Considering that the dietary burden of ruminants and pigs is triggered, investigation on the fate of residues in these animals is necessary. During the peer review of exprephon, a metabolism study was assessed where lactating goats were dosed with 0.37 and 0.46 mg/kg bw/d of 14C-ethephon, corresponding to the N and 8N expositre of meat ruminants A he Netherlands, 2004). This study demonstrates that the parents compound is hadrolysed to lose its chlorine and phosphate groups and that the carbon units are taken up into the Fricarbaylic acid cycle to yield natural products like fat, protein, carbolizarate and CO2. Ethephon and HEPA afterpreted to be the only toxicologically relevant compounds and the highest addioactive residing level was found in liver (1 mg/kg) of which 0.15% was considered ethernon and/or HERA (max. 0.0015 mg/kg). Since metabolism in rats and ruminants was demonstrated to be similar the findings in ruminants can also be extrapolated to pigs. Based on these data and the fact that residues in all ruminant commodities were expected to be very low, no residue definition was proposed in the framework of the peer review (EFSA, 2008a). In the framework of this review, however Additional crops contribute to the dietary burden of livestock resulting in a higher exposure of livestock to ethephon residues and the necessity to establish a residue definition in pigs and ruthinants. Also in Contrast to the peer review, data are now available indicating that HEPA is Expected to result in adorse effects at much higher exposure levels than ethephon (see also section 2). Therefore, the relevant residue in pigs and ruminants is now defined as ethephon, both for enforcement and risk assessment purposes.

For poultry there is in principle no necessity to establish a residue definition because the calculated dietary burden of poultry to ethephon residues amounted to less than 0.1 mg/kg DM. Nevertheless, a metabolism study with laying hens is reported in the DAR on ethephon. This study demonstrates that metabolic pathways of ethephon in ruminants and poultry are very similar (The Netherlands, 2004). It is therefore concluded that the relevant residue in poultry could also be defined as ethephon, provided that the use of ethephon is supported on additional crops resulting in a higher exposure of poultry to ethephon residues. In the meantime, a residue definition for poultry products is not required.



The above considerations and conclusions are still considered valid except that a cotton metabolism study is now available and its results are in line with those of the wheat and tomato metabolism studies (refer to CA 6.2.1). Therefore, the provisional residue definition in food commodities of plant origin is confirmed and can be considered "final". Furthermore, the exposure level that makes it necessary to investigate the nature and level of residues in food of poultry origin is now exceeded (refer to CA 6.4). Therefore, it is appropriate to set a residue definition for ethephon in food of poultry origin.

In summary the proposed residue definition of ethephon in food and feed of plant and animal origions parent ethephon. This residue definition applies to MRL setting / enforcement and to risk assessment as well.

Table 6.7.1-1 Proposed residue definition of ethephop

Commodities	MRL setting Enforcement
Food / feed of plant origin	Edephon Fibephon
Food of animal origin	Ethephon

CA 6.7.2 Proposed MRLs and justification of the acceptability of the levels proposed

The existing EU MRLs for ethephon in barley grain, wheat grain and food commodities of animal origin are shown in Table 6.7.2-, 100

Table 6.7.2-1: Current FO MRL of etherhon relevant to the representative uses of the active substance as an anti-lodging agent in barley and wheat

Code	4	Commodity	MRL (mg/kg)
0500010		Barley (grain)	1
0500090		Wheat Ograin)	1
1000000	Products of	Danimal origin - terrestrial animals	0.05*

An overview of the available residue data that support the representative uses of ethephon as an antilodging agent in barley and wheat's given in Table 6.7.2-2. For both barley grain and wheat grain 8 trials are available from each zone to derive an MRL. Currently no MRLs are set for straw but theoretically the same number of data would be available to derive MRLs for ethephon in straw.

Overall, higher levels of ethephon residues were found in barley and wheat grain samples from the northern zone than in barley and wheat grain samples from the southern zone. This is an expected result since the supported GADs are different for the two zones. In the northern zone the compound may be applied up the growth stage BBCH 51 while in the southern zone the latest growth stage for application is BBCH 39. Consequently, it is appropriate to derive the MRLs for ethephon in barley grain and wheat grain from the data generated in the northern zone. Using the OECD MRL calculator an MRL of 1.5 mg/kg is derived for barley grain based on the residue data generated for wheat grain based on the residue data generated for wheat grain in the northern residue zone.

However, since application is performed before the development of grain and according to the guideline SANCO 7525/VI/95 - rev.9, it is possible to extrapolate between barley and wheat. Furthermore, according to both the Mann-Whitney U-test and the Kruskal-Wallis H-test, the residue



data for the two crops are likely to belong to similar distributions and it may, therefore, be justified to combine the two residue datasets to calculate a common MRL for ethephon in barley and wheat grain. Using this approach, an MRL of 0.9 mg/kg is derived.

Both approaches (derivation of different MRLs for each crop based on the respective datasets or derivation of a common MRL based on the combined datasets) are scientifically justifiable. The first option would make it necessary to increase the current EU MRL for ethephon in barley (grain) from 1 mg/kg to 1.5 mg/kg while the second option would not make it necessary to modify the existing MRLs for ethephon in barley (grain) and wheat (grain). In the following it is assumed that based on the representative uses in barley and wheat it is suitable to see common MRL of 0.9 mg/kg for ethephon in barley and wheat grain. However, the other approach would also be possible and would not change the conclusions of the consumer risk assessment. Notice bly, in the context of the periodic review of the Codex MRLs of ethephon, the JMPR 2015 favoured the approach which consists in setting different MRLs for barley and wheat grain.

Table 6.7.2- 2: Overview of the available residue trial data to support the representative uses of ethephon as an anti-lodging agent in barley and wheat

				(7x)	
Commodity	Residue region	Individual trial vsults - Thephop@mg/kg/\$	STMR (ing/kg)	JJR Gag/kg)	Calculated MRL* (mg/kg)
Barley grain	NEU	0.031, 0.067, 0.090, 0.13, 0.16(0.23, 0.0), 0.73	0.150	0.73	1.5 (1.167)
Wheat grain	NEU	0.052, 0.059, 0.059, 0.083, 0.11, 0.44, 0.23, 0.31	0.097	0.31	0.5 (0.505)
Cereal grain	NEU	0.030, 0.052, 0.059, 0.059, 0.067, 0.083, 0.090, 0.00, 0.13, 0.14, 0.16, 0.23, 0.23, 0.31, 0.41, 0.43,	0.12	0.73	0.9 (0.900)
Barley grain	SEU É	0.021, 0.034, 0.035, 0.039, 0.041, 0.047, 0.14, 0.21	0.040	0.21	0.4 (0.340)
Wheat grain	SEU	0.000, 0.011, 0.025, 0.043, 0.049, 0.055, 0.10,	0.046	0.13	0.3 (0.223)
Cereal grain	SEU	0.010, 0.011, 0.021, 0.025, 0.034, 0.035, 0.039, 0.041, 0.043, 0.047, 0.049, 0.057, 0.10, 0.13, 0.14, 0.21	0.042	0.21	0.3 (0.283)
Barley straw	MEU	©35, 0,45, 0.51, 664, 0.78, 1.2, 1.5, 3.6	0.71	3.6	6 (5.426)
Wheat straw	NEG	0.36, 0.44, 657, 0.66, 1.2, 1.2, 1.3, 1.5	0.93	1.5	3 (2.795)
Cereal straw	NEU Q	@:35, 0.36, 0.43, @44, 0.51, 0.57, 0.64, 0.66, 0.78, 2, 1.2, 2, 1.3, 1.5, 1.5, 3.6	0.72	3.6	5 (4.224)
Barley straw	SEU	0.23, 0.24, 0.35, 0.39, 0.39, 0.97, 1.1, 1.7	0.39	1.7	3 (2.795)
Wheat straw	SEU	0.21, 0.29, 0.30, 0.44, 0.84, 0.86, 1.2, 1.7	0.64	1.7	3 (2.827)
Cereal straw	SEU	0.21, 0.23, 0.24, 0.29, 0.30, 0.35, 0.39, 0.39, 0.44, 0.84, 0.86, 0.97, 1.1, 1.2, 1.7, 1.7	0.42	1.7	3 (2.743)

^{*} The MRLs were estimated based on the OECD MRL calculator. The values in brackets correspond to the calculated values before rounding to the appropriate MRL classes.



The highest residues of ethephon in food commodities of animal origin that might result from the herein supported representative uses were estimated and the appropriate MRLs were derived under Point CA 6.4. A comparison of these MRLs with the current EU MRLs for ethephon in food commodities of animal origin is provided in Table 6.7.2-3. Except for kidney of sheep all the MRLs derived based on the representative uses are below the current EU MRL of 0.05 kg/kg.

Table 6.7.2-3: EU MRLs for ethephon in food of animal origin: current values and values derived based on the representative uses

Food commodity	Current EU MRL (mg/kg)	MRL derived based on the representative uses (mg/kg)	Comment
Swine - muscle	0.05*	0.20	See CA 6.4.3
Swine - fat tissue	0.05*	Q.01 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	SCCA 6 AS
Swine - liver	0.05*	Q0.01	See CA 6.4.3 0
Swine - kidney	0.05*	2 0.00 C	See OX 6.4.307
Bovine - muscle	0.05*	0.01	See CA 6.02
Bovine - fat tissue	0.05*	0.01	See CA:6.4.2 @
Bovine - liver	0.05*	0.01	See CX 6.4.2
Bovine - kidney	0.05*	0.04	See CA 6.#2
Sheep - muscle	0.05*	√ ×0.01 °	See CA 6.4.2
Sheep - fat tissue	0.03*	\$ 0.0k	See &A 6.4.2
Sheep - liver	Ø.05* O	6,02	Se&CA 6.4.2
Sheep - kidney	Ø 0.05%	§ 0.07	ee CA 6.4.2
Poultry - muscle	0.05*	0.00	See CA 6.4.1
Poultry - fat tissue	0.05*	Ø01 Ø	See CA 6.4.1
Poultry - liver	0.05*	90.01 S	See CA 6.4.1
Poultry - kidney	0.05*		LOQ - not investigated in feeding studies
Milk - cattle	0 _{0.05*} 0° 5	0.01	See CA 6.4.2
Milk - sheep		0.01	See CA 6.4.2
Bird eggs - chicken	Ø 0.05*	0.01	See CA 6.4.1

CA 6.7.3 Proposed MRLs and justification of the acceptability of the levels proposed for imported products (import tolerance)

No import tolerances are opplied for in the context of this re-approval dossier. However, according to Article 14 of Regulation EC No 396/2005, the existing Codex MRLs have to be taken into account when setting EU MR.

CA 6.8 Proposed safety intervals

The application time for the use of ethephon in cereals to prevent lodging is expressed in terms of growth stage. Treatment may be conducted up to the growth stage BBCH 51 in the northern part of Europe and up to the growth stage BBCH 39 in the southern part of Europe.

In the 16 trials conducted in the northern part of Europe, the interval between application and harvest ranged between 54 days and 78 days. The highest residue of 0.73 mg/kg in grain was observed in trial in which harvest was conducted 56 days after application but two other trial with a comparable interval between application and harvest (55 and 56 days, respectively) showed rather tow residues (0.067 mg/kg and 0.09 mg/kg). Therefore, intervals of less than 60 days between application and harvest do not necessarily imply high residue levels.

In the 16 trials conducted in the southern part of Europe, the interval between polication and parvest ranged between 58 days and 110 days. The residues in mature grain Highest residue of 0.21 mg/kg) were far below the MRLs proposed based on the representative use for the northern part of Europe.

Based on these considerations it is not deemed necessary to see a minimum interval between treatment of cereals with ethephon and harvest of grain and straw. Adherence to the GAP growth stages should ensure that the residues in treated grain do not exceed the proposed MRLs.

In Europe, immature cereals are normally notoed to livestock. Therefore, no waiting period before feeding treated cereals to livestock is proposed.

CA 6.9 Estimation of the potential and actual exposure through diet and other sources

The toxicity endpoints considered for the dietary risk assessment are shown in Table 6.9-1. Detailed justification for these proposals is provided in Section of this dossier.

Table 6.9- 1:	* Toxicity endpoints	s considered for	the d ietary r	risk assessment
----------------------	----------------------	------------------	-----------------------	-----------------

Endpoint	wee/kg bw/day)	Source	Safety factor
ADI		90 day dog study	100
ARfD	20.05	28 days or dog study (AChE inhibition), lowered to get a 10 dold MoS to the NOAEL from human data	100

In the context of this cossier for the renewal of the approval of ethephon, the dietary risk assessment was limited to the residues well to result from the representative uses. As shown in Table 6.9-2 the chronic exposure was estimated based on the median residue levels in food of plant and animal origin while for the acute exposure the righest residues were taken into account. For barley and wheat grain the median and highest residue values were derived from the combined residue dataset for the two crops in the northern residue zone, which is consistent with the proposed approach for MRL setting.

All calculations were performed using the revision 2 of the EFSA Pesticide Residues Intake Model (PRIMo 2). The outcome of the chronic and acute dietary risk assessments is shown in Table 6.9-3 and Table 6.9-4, respectively. The highest IEDI was estimated to be 5.6% of the ADI (for the WHO cluster diet B) while the highest IESTI was 21.1% of the ARfD (due to consumption of wheat by children). It may be concluded that the representative uses supported for the renewal of the approval



of ethephon do not result in chronic or acute consumer exposures exceeding the respective toxicological endpoints. Therefore, these uses do not cause chronic or acute health concerns for consumers.

Table 6.9- 2: Residue values considered for the dietary risk assessment (Residue definition for dietary risk assessment: parent ether hon)

	Chron	nic risk assessment		te risk assessment
Commodity	Residue level (mg/kg)	Comment (Residue level (mg/kg)	Comment
Barley grain	0.12	STMR for cereals in the northern zone	9.73	HR for ereals in the northern zone
Wheat grain	0.12	STMR for cereals in the northern zone		HP for cereals in the northern zone
Swine - muscle	0.01	Median residue	3 0.01	Maximum residue*
Swine - fat tissue	0.01	Median residue*	0.010	Maximum residue*
Swine - liver	0.01	Median residue*	9.01	Maximun residue*
Swine - kidney	0.01	Median residue*	Ø.01 , V	Maximum residue*
Bovine - muscle	0.01	Median residue*	₹ <u>0</u> .0¥	Maximum residue*
Bovine - fat tissue	0.01	Median residue*		Maximum residue*
Bovine - liver	0.01	Median residue	Ø.01 🦠	Maximum residue*
Bovine - kidney	0.01	Median residue	® 0.04	Maximum residue
Sheep - muscle	0.04	Median residue* >	0.01	Maximum residue*
Sheep - fat tissue	Ø.01 Q	Median residue	20 ,01	Maximum residue*
Sheep - liver	0.01	Medran residue*	\$\int 0.01	Maximum residue
Sheep - kidney	0.02	Median residue	0.07	Maximum residue
Poultry - muscle		Median residue	0.01	Maximum residue*
Poultry - fat tissue	0.01	Median residue*	0.01	Maximum residue*
Poultry - liver	F 0,64 4	Median residue*	0.01	Maximum residue*
Poultry - kidney	0.01	Median residue*	0.01	Maximum residue*
Milk - cattle	0.01	Median residue*	0.01	Maximum residue*
Milk - sheep	0.01	Median residue*	0.01	Maximum residue*
Bird eggs - chicken	0 .01	Median residue*	0.01	Maximum residue*

^{*} Rounded to the LOQ of enforcement method.

Table 6.9-3: Chronic risk assessment according to PRIMo 2 for the representative uses of ethephon

IEDI (0/ ADI)	MC D.	Highest	contributor to IEDI		
IEDI (% ADI)	MS Diet	(% ADI)	Commodity		
5.6	WHO Cluster diet B	5.1	Wheat _ °		
4.5	NL child	2.8	Wheat © Q		
4.4	WHO cluster diet D	3.9	What A		
4.0	IT kids/toddler	4.0	Wheat O S		
3.5	ES child		,Wheat		
3.4	DK child	3.3	Wheat &		
3.3	DE child	2.5	Wheat C		
3.2	WHO cluster diet E	2.4	Wheat S		
2.9	WHO Cluster diet F	\$\frac{1}{2}.2	Wheat		
2.6	SE general population 90th percentile	© 1.9∜√	Wheat 🛇		
2.5	IT adult	25	Wheat		
2.4	WHO regional European diet	€1.8 ×	Whean		
2.4	UK Toddler	2.4	Woeat		
2.4	PT General population The Property of the Prop		Wheat		
2.4	IE adult	M.4	Wheat		
2.2	FR all population	2.0	Wheat		
2.1	ES adult		Wheat		
1.9	NL generated and the second se	2.2	Wheat		
1.9	FR infant	1.3	Cattle Milk		
1.8	FR fooddler	1.6	Wheat		
1.6	UK Infant O V S O	1.6	Wheat		
1.3	VK vegetarian	1.2	Wheat		
1.3	DK-Qult O O V	1.2	Wheat		
1.0	UK Adulta O C	1.0	Wheat		
1.0	T adult	0.6	Wheat		
0.6	FI adult & S	0.6	Wheat		

Table 69-4: Acute wisk assessment according to PRIMo 2 for the representative uses of etheption

	Children A	Adults			
IESTI (% ARf	Commodity	IESTI (% ARfD)	Commodity		
21.1	Woreat	11.4	Wheat		
2.6	Barley	10.6	Barley		
2.5	Cattle Milk	0.3	Cattle Milk		
0.3	Bovine: Kidney	0.2	Poultry: Meat		
0.3	Bovine: Meat	0.1	Bovine: Kidney		



CA 6.10 Other studies

CA 6.10.1 Effect on the residue level in pollen and bee products

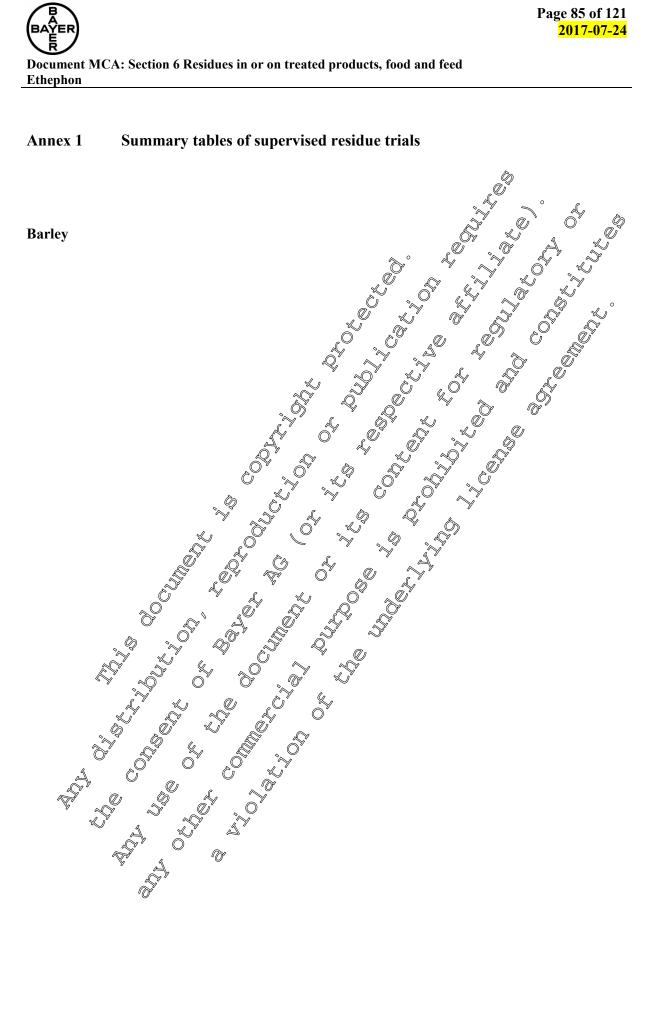
No suitable test method for the determination of residues in pollen and bee products is listed in Commission Communication 2013/C 95/01 about the implementation of Regulation (EU) No. 283/2013. Therefore, this point does not need to be addressed at the current stage. According to the EFSA Guidance Document on the risk assessment of plant protection products on bees [EFSA Journal 2013;11(7):3295], barley and wheat do not produce nectar and in general they are considered of low attractiveness to bees for pollen although the collection of pollen cannot be excluded.

However, for the evaluation of residues in pollen and be products for human consumption, the relevant question regarding bee attractiveness is not whether or not the crop is occasionally visited by bees, but if the crop is foraged by honey bees to an extent of conomic relevance. A relevant residue level in pollen (and bee products) is only likely to occur if a significant portion of rollen (and nectar) is collected from treated cereal fields by a whole colony. The guidance Document clearly indicates that this is not the case.

that this is not the case.

It may be concluded that under normal conditions the herein supported representative uses of ethephon are very unlikely to result in significant levels of ethephon residues in pollen or other bee products.







RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	ATA FRO	M SUPERVIS	SED TRIA	ALS (SUMMA)	RY)	Active substance		:	ethephon			
(Application on agric Responsible body for Country Content of active sub Formulation Commercial product Producer of commer	cultural and ho reporting (na ostance (g/k (e.g	rticultural crops) me and address) g or g/L) . WP)		oScience AG, Monheir L 480	,	Crop/Crop Group Page Indoor/outdoor Other a.s. in formuland content) Residues determined Residues calculated	ation Common nan		Céreals 1- A Outdoor ethephon			
1	2	3	4	5		396	7 , 2	8.40	9,00	10		11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application per treatm	2	Dates of 🖔	Growth stage at last reatment	Portion analysed	Residués	DALT	1.	emarks
Year of Trial	(a)	(b)	(c)	kg Water	kg a.s./hL ((d) C			,	(f)		
13-2027 13-2027-01 2013 M-526906-01-1	Winter barley Duett	1) 01.10.2012 2) 07.06.2013 -12.06.2013 3) 01.07.2013 -31.07.2013	Spraying			24.05,2803	Spinning of Speading	green material grain straw	6.2 0.61 0.55 0.26 0.43 0.13 0.51	0 7 14 21 24 59	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
13-2027 13-2027-02 2013 M-526906-01-1	Winter barley Meridian	1) 28.09.2012 (2) 2) 01.06.2013 (3) 1.096.2013 (2) 29.07.2013 (2) 29.07.2013	Spraying	0.512 267 2.512 267	0.192	22.05.2013	Beginning of heading	green material grain straw	3.2 <0.05 0.067 0.35	0 33 55 55	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany (g/kg or g/L) : 480 g/L (e.g. WP) : 480 SL

Commercial product Producer of commercial product

Content of active substance

(name)

: Ethephon SL 480

: Bayer CropScience AG

Indoor/outdoor

and content) Residues determined as Residues galculated as

Active substance

Crop/Crop Group

Page

Cereals

2- A.
Ontdoor

ethephon

ethephon

Other a.s. in formulation common name

										Ğ	
1	2	3	4	5		\$ 9°6	7 1 1	8 &	9	10	11
Study Trial No.; Plot Location incl.	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering	Method of treatment	Application ra per treatment	~06 _A	Dates of treatment(s)/ Application interval	,SF 1/2	Pertion Surallysed	Residués Dag/kg)	DALTA days)	Remarks
postal code		3) Harvest 4) Transplanting		, \$		or no. of treatments and hast date/			99 ¹		
Year of Trial	(a)	(b)	(c)	kg Water a.s. (L/hax)	o≫ kg a.s./hI₄ (S (d) C				(f)	
13-2027 13-2027-03 2013 M-526906-01-1	Winter barley Malabar	1) 15.10.2012 2) 21.06.2013 - 01.07.2013 3) 22.07.2013 - 09.08.2013	Spraying		E. C	03.06.2803 03.06.2803 2.05.2013	Sepinning of Seading	green material grain straw	7.9 3.8 0.85 0.57 0.27 0.73	0 7 14 21 43 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2027 13-2027-04 2013 M-526906-01-1	Winter barley Cassata	16.08.2013 C	Spraying		90.24 EX	31.05.2013	Beginning of heading	green material grain straw	6.6 0.36 0.23 3.6	0 34 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	TA FRO	OM SUPERVIS	SED TRIA	ALS (SUMMARY)	Active substance		•	etnepaton			
(Application on agric Responsible body for Country Content of active sub Formulation Commercial product Producer of commercial	reporting (nastance (g/	kg or g/L) g. WP)	: Bayer Crop : Germany : 480 g/L : 480 SL : Ethephon S : Bayer Crop		Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name: and content) Residues determined as Residues calculated as HERA HERA HERA 11						
1	2	3	4	5	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 2	820	9,0	11 100		
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Dates of V	Growth stage at		Residues	DALTA days)	Remarks	
Year of Trial	(a)	(b)	(c)	kg Water & kg a.s./hL					(f)		
13-2027 13-2027-01 2013 M-526906-01-1	Winter barley Duett	1) 01.10.2012 2) 07.06.2013 - 12.06.2013 3) 01.07.2013 - 31.07.2013	Spraying	O48 300 0.16	24.05.2802	Beginning of Seading	green material	0.091 <0.05 <0.05 <0.05 <0.05	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg	
					20 62 05 2013	<i>b</i>	grain straw	0.019	59 59	(h) 0.01 mg/kg day 59: 0.013 mg/kg in control sample (h) 0.05 mg/kg	
13-2027 13-2027-02	Winter barley Meridian	1) 28.09 2012 2) 01 06.2013 30 15.07.2013 - 29.07.2013	Sprecing	0.512 267 1 0.192		Beginning of heading	green material grain	<0.05 <0.05 <0.01	0 33 55	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
M-526906-01-1		- 29.07.200.3					straw	<0.05	55	(h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	ATA FRO	OM SUPERVIS	SED TRIA	ALS (SUMMARY)	Active substance		:	ethephon			
(Application on agric Responsible body for Country Content of active sub Formulation Commercial product Producer of commer	cultural and less reporting (restance (g	orticultural crops) name and address) /kg or g/L) ng. WP)		oScience AG, Monheim L 480	Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues determed Residues calculated	ntičn (common naqual		Cércals 2- B Outdoor HERA HERA			
1	2	3	4	5	\$ 9°6	7 , 2	8 J C	9	10		11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Dates of 🖁	Growth Grage at last deteatment	Portion analysed	Residués	DALTA (days)		Remarks
Year of Trial	(a)	(b)	(c)	kg Water kg a.s./luly a.s./l	ht of	(e) 1			(f)		
13-2027 13-2027-03 2013 M-526906-01-1	Winter barley Malabar	1) 15.10.2012 2) 21.06.2013 - 01.07.2013 3) 22.07.2013 - 09.08.2013	Spraying	Q8 300 0.16		Seginning of Seading	green material	0.094 0.088 0.085 0.076 0.059	0 7 14 21 43	(g) 01429 (h) 0.05 mg/kg	
						· V	grain straw	0.086	56 56	(h) 0.01 mg/kg (h) 0.05 mg/kg	
13-2027 13-2027-04	Winter barley Cassata	16.08.2013	Spraying	0.48 200 9.24	31.05.2013	Beginning of heading	green material grain	0.093 <0.05 0.055 0.066	0 34 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
2013 M-526906-01-1		10.06.2013 @					straw	0.000	08	(h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

Content of active su Formulation Commercial produc Producer of comme	(e.g	. WP) :	: 480 g/L : 480 SL : Ethephon SI : Bayer Crop			Indoor/outdoor Other a.s. in formuland content) Residues determine Residues calculated	ntion Common nan	POP:	cthephon cthephon			
1	2	3	4	5		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7.	8 & @	9,01	10	0	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application ra		Dates of treatment(s)/ Application interval or no of treatment(s) and as date/	Growth stage at last decatment	Pertion analysed	mg/kg)	DALTA (days)		Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s. ha (L/hax)	kg a.s./hI				7	(f)		
2014 M-533473-01-1	Winter barley Naomie	1) 24.09.2013 2) 21.05.2014 - 24.05.2014 3) 15.07.2014 - 17.07.2014	Spraying		0.16	29.04.2004	Seginning of Seading	green material grain	6.2 0.50 0.29 0.17 0.086	0 7 14 21 36 78	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
		W.						straw	0.64	78	(h) 0.05 mg/kg	
4-2022 4-2022-02 2014	Winter barley Leibnitz	1) 26.09.2013 2) 05.05.2014 - 09.05.2014 3,000.07.2014 2,5.07.2014		0.48)0.16 K)	30.04.2014	Beginning of heading	green material grain	7.7 0.37 0.41	0 21 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
A-533473-01-1 a) According to C b) Only if relevan	odex (or other e.g	. EU) Classification/Gu	jee variation of the state of t	COUNTERCY.		(f) DALT : Days (g) Reference to a	after last treatment.	straw	1.2	64	(h) 0.05 mg/kg	

Unity if relevant.

High or low volume spraying, spreading, design etc. overall broadcast.

Vear must be indicated. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

(Application on agric Responsible body for Country Content of active sub Formulation	reporting (narestance (g/k (e.g.	ne and address) g or g/L) WP)	: Bayer Crop : Germany : 480 g/L : 480 SL : Ethephon S	Science AG, Monheim		Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues determed	ntièn common nân		Cereals 2- A Ontdoor ethenhon ethenhon			
Producer of commer			: Bayer Crop			Residues calculated	as a s	© :	etheparon			
1	2	3	4	5		\$ 9°6	7 5	8 $_{\hspace{-0.1cm}\cancel{\hspace{-0.1cm}\nearrow}}$ $\mathbb C$	9	10	0 11	
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment		\$0 ^{\$} \$	Dates of treatment (s)/ Application interval or no, of treatments and	,S F V		Residues	DALA, Marian (Carlot)	Remarks	
Year of Trial	(a)	(b)	(c)	kg Water (L/hax)	≫ kg a.s./hI₄ ((e) 1 D			(f)		
14-2022 14-2022-03 2014 M-533473-01-1	Winter barley Obite	1) 03.10.2013 2) 30.04.2014 - 07.05.2014 3) 15.06.2014 - 30.06.2014	Spraying	088° 300°° 0	16	23.04.2014	Bearing of Seading	green material grain straw	6.6 0.34 0.15 0.10 <0.05 0.090	0 7 14 21 28 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
14-2022 14-2022-04 2014 M-533473-01-1	Winter barley Cassatta	1) 01.10.2013 \$\frac{1}{2}\$ 02.06.2014 \$\frac{1}{2}\$ 07.2014 \$\frac{1}{2}\$ 08.08.2014	Spraying		124 EX	13.05.2014	Middle of heading	green material grain straw	7.3 0.13 0.16 0.78	0 34 73 73	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg day 73: 0.088 mg/kg in control samp	ple

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant.

Unity it relevant.

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

RESIDUE DA	TA FRO	M SUPERVIS	ED TRL	ALS (SUMMAR)	Y)	Active substance		:	ethephon		
(Application on agric Responsible body for Country Content of active sub Formulation	cultural and ho reporting (na estance (g/k (e.g	rticultural crops) me and address) g or g/L) , WP)	: Bayer Cro : Germany : 480 g/L : 480 SL	pScience AG, Monheim	-,	Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content)	atišu kommon nžų		Cereals 1- B Outdoor		11 Remarks
Commercial product Producer of commer		,	: Ethephon S	SL 480 pScience AG		Residues determined	d as		HERA &		
- Troducer of commer	ciai product	•	. Dayer Cro	psciciic AG				© : <u>"</u>		, Ġ ^v	
1	2	3	4	5		\$ 0°6	7 , 2	826	9	10	. 11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Method of treatment	Application raper treatmen	it COPI	Dates of treatment(s)/ Application interval or no of	las Greatment	PILIOII	Residués Dag/kg)	DUM.	Kemarks
Year of Trial	(a)	4) Transplanting (b)	(c)			treatments and hast date/			, O. O.	(f)	
Tour of Thur	(u)	(6)	(6)	kg Water (L/hay	a.s./hl					(1)	
14-2022 14-2022-01 2014	Winter barley Naomie	1) 24.09.2013 2) 21.05.2014 - 24.05.2014 3) 15.07.2014	Spraying	G37 360	E>	N 3,5	Bearining of Seading	green material	0.12 <0.05 <0.05 <0.05	0 7 14 21	(g) 01429 (h) 0.05 mg/kg
M-533473-01-1		- 17.07.2014		of Bay		20.04.2014		grain straw	<0.05 0.016 0.055	36 78 78	(h) 0.01 mg/kg (h) 0.05 mg/kg
14-2022	Winter	1) 26.09.2013	Spraying	0.48	0.16	30.04.2014	Beginning of	green	0.12	0	(g) 01429
14-2022-02	barley	2) 05.05.2014	Spidyang	0.40	7	0.04.2014	heading	material	< 0.05	21	(h) 0.05 mg/kg
2014	Leibnitz	15 07 2014	1 6		OF Kr			grain	0.055	64	(h) 0.01 mg/kg day 64: 0.054 mg/kg in control sample
M-533473-01-1		13.07.2014 ©						straw	0.063	64	(h) 0.05 mg/kg day 64: 0.061 mg/kg in control sample

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany Content of active substance (g/kg or g/L) : 480 g/L : 480 SL (e.g. WP)

Commercial product : Ethephon SL 480 (name)

Producer of commercial product : Bayer CropScience AG Active substance

Crop/Crop Group 2-B Outdoor Page Indoor/outdoor

Other a.s. in formulation common name and content)

Residues determed as Residues calculated as

	>	NON	•	~ 1 ⁸
	HERA ®		0 2	
,	HEPA			

Study Trial No.; Plot Location incl. postal code Year of Trial (a) (b) (c) (c) (d) (d) (d) (d) (e) (d) (e) (d) (e) (d) (e) (e							M				.S	
Study Trial No.; Plot Location incl. postal code Year of Trial (a) (b) (c) (c) (d) (d) (d) (d) (e) (d) (e) (e	1	2	3	4	5		\$ 9°6	7 , 2	8 / 6	9.0	10	11
1.0cation incl. 2) Flowering 3) Harvest 4) Transplanting 4) Transplanting 4) Transplanting 5							Dates of	Growth stage at	Pertion	Residues	DALT	Remarks
Cocation incl. 2) Flowering 3) Harvest 4) Transplanting 4) Transplanting 4) Transplanting 5		/ Variety		-	per treatmen	t 🔊	treatment(s)/	last treatment	Sphallysed _	(mag/kg)		
Cocation incl. Prowering Section Cocation incl. Prowering Section Cocation Cocation				treatment			Application interval	\$ ×			(days)	
Year of Trial (a) (b) (c) kg a.s./hl. (d) (e) (a) (f) 14-2022 Winter barley 1) 03.10.2013 Spraying Object 23.04.2014 Deginning of beading Green material <0.05						•			A .			
Year of Trial (a) (b) (c) kg a.s./hl. (d) (e) (a) (f) 14-2022 Winter barley 1) 03.10.2013 Spraying Object 23.04.2014 Deginning of beading Green material <0.05	postal code		,									
Year of Trial (a) (b) (c) kg Water a s./hL (d) (e) (a) (f) (f) (14-2022 Winter barley 2) 30.04.2014 Spraying Obite -07.05.2014 3) 15.06.2014 Spraying Obite -07.05.2014 3) 15.06.2014 Spraying Obite -07.05.2014 Spraying Obite			4) Transplanting		<i>y</i> .	~ Ĉ	and Ager date/			0> 2		
14-2022 Winter barley 10 3.10.2013 Spraying 10 8 300 0 16 23.04.2014 Spraying of barley 20 30.04.2014 00 00 00 00 00 00 00	Year of Trial	(a)	(b)	(c)	kg Water -	lo ko			(a)©			
Obite -07.05.2014 3) 15.06.2014 30 15.06.2014	Tour or Trial	(4)	(0)	(6)	a.s. ha (L/ha)	a.s./hl			. 0.11		(1)	
Obite -07.05.2014 3) 15.06.2014 30 15.06.2014	14-2022	Winter	1) 03.10.2013	Spraying	441)5	0.16	23.04.2014	Reginning of	green	< 0.05	0	(g) 01429
	14-2022-03	barley	2) 30.04.2014	A C				Beading		< 0.05		(h) 0.05 mg/kg
		Obite	- 07.05.2014			The second		- Ó				
$\frac{1}{2014}$			3) 15.06.2014									
			- 30.06.2014)			- SU 4	J >		< 0.05	28	
M-533473-01-1 grain 0.021 56 (h) 0.01 mg/kg	M-533473-01-1		<i>y</i>			S.	10° -«'»	<i>b</i>	grain	0.021	56	(h) 0.01 mg/kg
				2 D		1 .49	× 20"		8			
			¥ .				700		straw	< 0.05	56	(h) 0.05 mg/kg
14-2022 Winter 1) 01.10.2013 Spraying 0.48 200 0.24 13.05.2014 Middle of heading material 0.050 34 (h) 0.05 mg/kg	14-2022	Winter	1) 01.10.2013	Spraying	0.48	0.24	13.05.2014	Middle of	green	0.072	0	(g) 01429
114-7077-04 I DATIEV 17107 OD 7084 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7 8 7 I 7	14-2022-04	barley	2) 02.06.2014			1 ~~~		heading		0.050	34	(h) 0.05 mg/kg
Cassatta - 19:\$00.2014		Cassatta	- 10.406.2014		2 () ·		1			0.047	72	4) 0.01 //
grain 0.047 73 (h) 0.01 mg/kg day 73: 0.011 mg/kg in control sample			301507.2014	* [grain	0.04 /	13	
37.507.2014			€ 208.08.2014 €	Or		P ″						day 73: 0.011 mg/kg in control sample
straw <0.05 73 (h) 0.05 mg/kg			N.C	. e,					straw	< 0.05	73	(h) 0.05 mg/kg
2014			K. J. S.)								
M-533473-01-1	M-533473-01-1		4									

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant.

Only if relevant.

High or low volume spraying, spreading, degring etc. overall broadcast. (c)

(d) Year must be indicated.

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- Limit of quantification (h)
- (i) Dosage of a.s. or water given as...
- Missing data in the above columns occurs where the information is not available in the original report.



Any use of the document or its content to say the document of its content to say the say Document MCA: Section 6 Residues in or on treated products, food and feed Ethephon

According to Codex (or other e.g. EU) Classification/Guide.

(b)

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

EU) Classification Codo.

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RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany Content of active substance (g/kg or g/L) : 480 g/L (e.g. WP) : 480 SL

Commercial product

(name) Producer of commercial product

: Ethephon SL 480 : Bayer CropScience AG Active substance

Crop/Crop Group
Page
Indoor/outdoor
Other a.s. in formulation common name and content)
Residues determined as
Residues calculated as
Residues calculated as
Residues calculated as

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-	ì	1									<u> </u>	1
1	2	3	4		5		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 2	8, 6	9	10	11
Study Trial No.; Plot	Commodity / Variety	Date of 1) Sowing or planting	Method of treatment		Application ra per treatmen		Dates of treatment(s)/ Application interval		Pertion analysed	Residues Ong/kg)	DAL A	Remarks
Location incl. postal code		2) Flowering 3) Harvest 4) Transplanting			*. }\$		or noof treatments and					
Year of Trial	(a)	(b)	(c)	kg a.s. Ma	Water (L/hax)	Ø kg a.s./hL €	(d) C		(a). b'		(f)	
13-2028	Winter	1) 28.10.2012	Spraying	Ġ8°	300	0.16	25.04.2802	Flag leaf stage	green	4.5	0	(g) 01429
13-2028-01	barley	2) 07.05.2013	2		>				material	0.24	7	(h) 0.05 mg/kg
	Cervoise	- 17.05.2013 3) 03.07.2013	2 B	1	A.			Ó		0.15 0.092	12 21	
		- 10.07.2013		POR	al ^e					<0.05	39	
2013 M-529491-01-1					977		Poser,		grain	0.035	71	(h) 0.01 mg/kg
						-/OI @	av \		straw	0.23	71	(h) 0.05 mg/kg
13-2028	Winter	1) 10.12.2012 \$	Spraying	0.48	Q ₁₀₀	0.12	09.04.2013	Flag leaf stage	green	4.2	0	(g) 01429
13-2028-02	barley	2) 05.05.2013	Spraying		200	, N	09.04.2013		material	0.26	27	(h) 0.05 mg/kg
	Graphic	- 17 05.2013 3 12 06.2013 3 30.06.2013							grain	0.21	72	(h) 0.01 mg/kg
2013		I 🙈	*©	COLUM		Ų Ť			straw	1.7	72	(h) 0.05 mg/kg
M-529491-01-1			ď į	آ								

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

Country Content of active sul Formulation Commercial produc	(e.g	sg or g/L) : . WP) : . me) :	: Germany : 480 g/L : 480 SL : Ethephon S			Page Indoor/outdoor Other a.s. in formula and content) Residues determine Residues calculated	ation Common nan		Cereals 2- A Outdoor ethephon			
Producer of commer		1	: Bayer Crop			Residues calculated	√		europaon	\$\tag{\tag{\tag{\tag{\tag{\tag{\tag{	T	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	4 Method of treatment	Application raper treatmen	t COPI	Dates of treatment (s)/ Application interval or no of treatments and	Growth rage at lander at the contract of the c		Residués Dag/kg)			11 Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s. (L/hav	kg a.s./hI	(d) CC				(f)		
13-2028 13-2028-03 2013 M-529491-01-1	Winter barley Quench	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 15.06.2013 - 15.07.2013	Spraying		0.16	23.04.2803	The leaf stage 1	green material	5.9 0.44 0.087 0.078 0.051	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg	
vi-329491-01-1				OF PACUL			·	grain straw	0.041	62 62	(h) 0.01 mg/kg (h) 0.05 mg/kg	
3-2028 3-2028-04 2013 4-529491-01-1	Winter barley Federal	1) 07.11.2012 2) 30.04.2013 - 10.05.2013 20.5.06.2013	Spraying	0.48	9.137 S	24.04.2013	Flag leaf stage	green material grain straw	3.5 <0.05 0.021 0.24	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
a) According to C b) Only if relevan	odex (or other e.g	g. EU) Classification/Gui	ide.	COMMETCE CE			after last treatment.	Jan.	0.21	1	(.) 0.00 mg ng	

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

			ED TRIA	ALS (SUMMARY	Y)	Active substance		:	ethephon	• •	
(Application on agric Responsible body for Country Content of active sub Formulation	reporting (nai stance (g/k (e.g.	me and address) :: g or g/L) :: .WP) ::	Germany 480 g/L 480 SL	oScience AG, Monheim		Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content)	ation Common nan		Cereals 1- B Outdoor		
Commercial product Producer of commercial			Ethephon S Bayer Crop			Residues galculated	ı as	e, :	HEPA		9
1	2	3	4	5		1	7 , 3	826	9,0	10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application ra		Dates of 🖁	Growth stage at last treatment	Pertion	Residués Opag/kg)	DAL	Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s. (L/hav)	kg a.s./hI	(d) AC			,	(f)	
13-2028 13-2028-01 2013 M-529491-01-1	Winter barley Cervoise	1) 28.10.2012 2) 07.05.2013 - 17.05.2013 3) 03.07.2013 - 10.07.2013	Spraying		0.16	25.04.2863	The leaf stage	green material	0.053 <0.05 <0.05 <0.05 <0.05	0 7 12 21 39	(g) 01429 (h) 0.05 mg/kg
								grain straw	<0.01 <0.05	71 71	(h) 0.01 mg/kg (h) 0.05 mg/kg
13-2028 13-2028-02	Winter barley Graphic	1) 10.12.2012 (2) 2) 05.05.2013 (3) 206.2013	Spraying	0.48	9.12 (E)	99.04.2013	Flag leaf stage	green material	0.058 <0.05	0 27	(g) 01429 (h) 0.05 mg/kg day 0: 0.081 mg/kg in control sample
2013 M-529491-01-1	4	30.06.2013 30.06.2013						grain	0.069	72	(h) 0.01 mg/kg day 72: 0.023 mg/kg in control sample
			L					straw	0.17	72	(h) 0.05 mg/kg day 72: 0.17 mg/kg in control sample

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany Content of active substance (g/kg or g/L) : 480 g/L (e.g. WP) : 480 SL

Commercial product

(name) Producer of commercial product

: Ethephon SL 480 : Bayer CropScience AG

Active substance

Crop/Crop Group
Page
Indoor/outdoor
Other a.s. in formulation common name
and content)
Residues determined as
Residues calculated as a HEPA
HEPA

Residues calculated as

D	HELA
9	HEPA
	A Property

						10 ¹⁰				, S	
1	2	3	4	5		\$ 9°6	M 7 1 1 1 1	826	9	10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment		~06J	Dates of	Growth stage at	Portion Canadysed	Residués Ong/kg)	DALTA (Paragraphy) (days)	Remarks
Year of Trial	(a)	(b)	(c)		kg a.s./hl	C (d) CC	(1) No.			(f)	
13-2028 13-2028-03 2013 M-529491-01-1	Winter barley Quench	- 15.07.2013	Spraying			23.04.2803	Fige leaf stage	green material grain	0.051 <0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 24 62	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg
		l ~ ~ ~	<u></u>		20 J.	1200		straw	0.054	62	(h) 0.05 mg/kg
13-2028 13-2028-04 2013 M-529491-01-1	Winter barley Federal	05.07.2013	Spraying	0.48 9550 V	137 E	24.04.2013	Flag leaf stage	green material grain	<0.05 <0.05 0.070	0 29 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 64: 0.060 mg/kg in control sample
			<u></u>					straw	< 0.05	64	(h) 0.05 mg/kg

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

RESIDUE DA (Application on agric Responsible body for Country Content of active sub Formulation	cultural and how reporting (namestance (g/k	rticultural crops) me and address) g or g/L)		ALS (SUMMA) pScience AG, Monheir	,	Active substance Crop/Crop Group Page Indoor/outdoor Other a.s. in formula	atisu common usu	· · · · · · · · · · · · · · · · · · ·	cthephon ethephon		T X.CG	
Commercial product Producer of commerc			: Ethephon S	SL 480 pScience AG		Indoor/outdoor Other a.s. in formuland content) Residues determined Residues calculated	d as a second	e. : **	ethephon ethephon			
1	2	3	4	5		1 % 0) 6 a	7			10		11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application per treatm	2	Dates of treatment(s)/ Application interval or no.of treatments and ast date/	Growt Grage at	Pertion	Residués Jung/kg)	DALT		Remarks
Year of Trial	(a)	(b)	(c)	kg Water	kg a.s./hI	(d) C			,	(f)		
14-2020 14-2020-01 2014 M-533463-01-1	Winter barley Limpid	1) 13.10.2013 2) 22.04.2014 - 29.04.2014 3) 17.06.2014 - 30.06.2014	Spraying	2000	0.14	08.04.2804	The leaf stage '	green material grain straw	5.6 3.0 3.0 0.38 0.095 0.14	0 7 14 21 42 72	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
14-2020 14-2020-02 2014 M-533463-01-1	Winter barley Graphic	1) 20.11.2013 2) 20.04.2014 - 27.94.2014 3 10.06.2014 2 10.07.2014		0.411 942 C	0 12 KX	08.04.2014	Mid boot stage	green material grain straw	6.6 0.36 0.039 0.97	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

DALT: Days after last treatment.

Reference to analytical method. (g)

(h) Limit of quantification

Dosage of a.s. or water given as... (i)

Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	ATA FRO	M SUPERVIS	SED TRIA	ALS (SUMMARY)	Active substance		:	ethephon ethephon ethephon		
(Application on agric Responsible body for Country Content of active sul Formulation Commercial product Producer of commer	cultural and hor reporting (na ostance (g/	orticultural crops) ame and address) kg or g/L) g, WP) ame)		oScience AG, Monheim SL 480	Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues determined Residues calculated					
1	2	3	4	5	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 5	8 J C	9,0	10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Dates of 🖁	Growth stage at last treatment	Portion On allysed	Residués Opag/kg)	DALTA Ways)	Remarks
Year of Trial	(a)	(b)	(c)	kg Water & kg a.s.th. (L/hax) a.s./hl. (\mathcal{L} (d) \mathcal{L}				(f)	
14-2020 14-2020-03 2014 M-533463-01-1	Winter barley Lutece	1) 04.11.2013 2) 17.04.2014 - 27.04.2014 3) 05.06.2014 - 15.06.2014	Spraying		10.04.2804	The leaf stage	green material grain straw	3.3 1.2 0.34 0.10 <0.05 0.047	0 6 14 20 29 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2020 14-2020-04 2014 M-533463-01-1	Winter barley Mucho	1) 23.10.2013 2) 29.04 2014 - 03.05.2014 20.206.2014	Spraying		08.04.2014	Flag leaf stage	green material grain straw	8.2 <0.05 0.034 0.35	0 48 63 63	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

(Application on agric Responsible body for Country Content of active sub Formulation Commercial product Producer of commer	reporting (na ostance (g/l (e.g	nme and address) kg or g/L) z. WP) ame)	: Bayer Crop : Germany : 480 g/L : 480 SL : Ethephon S : Bayer Crop					Cereals 1- B Outdoor HERA HERA) ^T eë	
1	2	3	4	5	96		W	// V			11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Dates of treatment (s)/ Application interval or no. of treatments and	, S F V	Portion On Manager 1	Residués Jag/kg)	DALTA Ways)		emarks
Year of Trial	(a)	(b)	(c)	kg Water Kg a.s./hk (L/hax) a.s./hk ((e) 1			(f)		
14-2020 14-2020-01 2014 M-533463-01-1	Winter barley Limpid	1) 13.10.2013 2) 22.04.2014 - 29.04.2014 3) 17.06.2014 - 30.06.2014	Spraying			Fig leaf stage	green material grain straw	0.069 0.055 0.055 <0.05 <0.05 0.026	0 7 14 21 42 72 72	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
14-2020 14-2020-02 2014 M-533463-01-1	Winter barley Graphic	1) 20.11.2013 \$\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	Spraying	0.411 942 9.12 	08.04.2014	Mid boot stage	green material grain straw	0.14 <0.05 0.013 0.080	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany Content of active substance (g/kg or g/L) : 480 g/L : 480 SL (e.g. WP)

Commercial product Producer of commercial product

(name)

: Ethephon SL 480 : Bayer CropScience AG Active substance

Crop/Crop Group

Page

Indoor/outdoor

Other a.s. in formulation common name

and content)

Residues determined as Residues calculated as

3 11 esidué. Dag/kg) Application rate Residues Study Commodity Date of Method Growth stage at Pertion Remarks Dates of DALT 1) Sowing or treatment(s)/ last treatment analysed Trial No.; / Variety per treatment of Application interval Plot planting treatment 2) Flowering Location incl. 3) Harvest postal code 4) Transplanting Year of Trial Water (f) (a) (b) (c) 14-2020 0 Winter 1) 04.11.2013 < 0.05 (g) 01429 Spraying 14-2020-03 barley 2) 17.04.2014 material < 0.05 6 (h) 0.05 mg/kg- 27.04.2014 < 0.05 14 Lutece 3) 05.06.2014 < 0.05 20 2014 - 15.06.2014 < 0.05 29 M-533463-01-1 < 0.01 grain 64 (h) 0.01 mg/kgstraw < 0.05 64 (h) 0.05 mg/kg 14-2020 0 Winter Flag leaf stage green 0.14 (g) 01429 2) 29.04.2014 14-2020-04 barley material < 0.05 48 (h) 0.05 mg/kgMucho grain 0.014 63 (h) 0.01 mg/kg 2014 straw < 0.05 63 (h) 0.05 mg/kg M-533463-01-1

According to Codex (or other e.g. EU) Classification/Guide.

(b)

Unity if relevant.

High or low volume spraying, spreading, daying etc. overall broadcast.

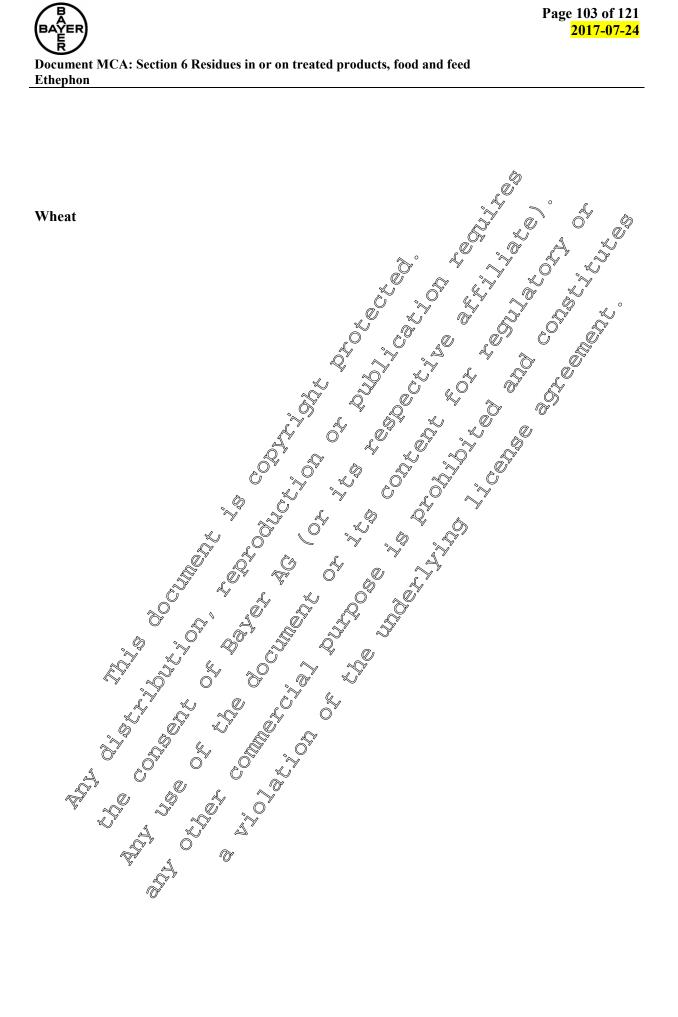
Vear must be indicated. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as...
- Missing data in the above columns occurs where the information is not available in the original report.







RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

(Application on agric Responsible body for Country Content of active sub Formulation	cultural and ho r reporting (na ostance (g/k (e.g	rticultural crops) me and address) g or g/L) . WP)		Science AG, Monheim	-,	Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues deterance	atičn Common nån		Cereals 1- A. Outdoor ethephon			
Producer of commer	cial product	,	: Bayer Crop	Science AG		Residues calculated	as J	© :	ethephon	STI		
1	2	3	4	5		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 3	8 & @	9,0	10	0	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment		t ÇÕŽ	Dates of treatment(s)/ Application interval or no of treatments and	\$ ×	Pertion	Residués Dag/kg)	DALT	1	Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s. (L/hax)	kg a.s./hI	(d) Ĉ [©]				(f)		
13-2029 13-2029-01 2013 M-529493-01-1	Soft wheat Winnetou	1) 29.10.2012 2) 17.06.2013 - 24.06.2013 3) 10.08.2013 - 31.08.2013	Spraying		0.16	10.06.280.3°	Spinning of Seading	green material grain straw	3.3 0.46 0.21 0.17 0.17 0.059 0.36	0 7 14 21 23 75	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
13-2029 13-2029-03 2013 M-529493-01-1	Soft wheat Matrix	1) 20.10.2012 (2) 2) 18.06.2013 (3) 07.2013 (3) 08.2013 (2) 12.08.2013 (3)	Spraying	0.48 900 ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° °)216 E	12.06.2013	Beginning of heading	green material	3.1 0.16 0.11 0.11 0.11	0 8 14 21 29	(g) 01429 (h) 0.05 mg/kg	
		1 12.00.2015 C						grain straw	0.059 0.66	61 61	(h) 0.01 mg/kg (h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany (g/kg or g/L) : 480 g/L (e.g. WP) : 480 SL

Commercial product

Content of active substance

(name) Producer of commercial product

: Ethephon SL 480 : Bayer CropScience AG Active substance

Crop/Crop Group

Page

Indoor/outdoor

Other a.s. in formulation common name and content)

Residues determined as

Residues calculated as

ethephon . 3 5 11 esidue. Jug/kg) Residues Study Date of Application rate Growth stage at Pertion DALT Remarks Commodity Method Dates of treatment(s)/ last treatment analysed Trial No.; 1) Sowing or per treatment / Variety of Application interval Plot planting treatment 2) Flowering Location incl. Tassification/Guide.

"assification/Guide.

"In the control of the postal code 3) Harvest Year of Trial (f) Reginning of 13-2029 7.5 0 (g) 01429 13-2029-04 0.32 38 (h) 0.05 mg/kgmaterial 0.11 74 (h) 0.01 mg/kg grain straw 1.3 74 (h) 0.05 mg/kg M-529493-01-1

According to Codex (or other e.g. EU) Classification/Guide. Only if relevant. (b)

Unity in relevant.
High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method.
- Dosage of a.s. or water given as...
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	ATA FRO	OM SUPERVIS	SED TRIA	ALS (SUMMARY	Y)	Active substance		:	ethephon			
(Application on agric Responsible body for Country Content of active sub Formulation Commercial product Producer of commer	cultural and lar reporting (in postance (good (doing to the control of the contro	norticultural crops) name and address) y/kg or g/L) e.g. WP) name)	: Bayer Crop : Germany : 480 g/L : 480 SL : Ethephon S	Bayer CropScience AG, Monheim Germany 480 g/L 480 SL Ethephon SL 480			Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name and content) Residues determined as Residues calculated as HEPA Dates of Growth stage at Portion Residue's DAL					
1	2	3	4	5		306	7 , 5	8 @	9.0	10		11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	y Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	15		Dates of treatment(s)/ Application interval or no, of treatments and	S Preatment	Sanariysed	// DWG 0 / K 0 1	DALTA (days)		Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s. (L/hav	Ø≻kg a.s./hI₄ (. 0 2		(f)		
13-2029 13-2029-01 2013 M-529493-01-1	Soft wheat Winnetou	1) 29.10.2012 2) 17.06.2013 - 24.06.2013 3) 10.08.2013 - 31.08.2013	Spraying		0.16	10.06,280.3	Beanning of Seading	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 23	(g) 01429 (h) 0.05 mg/kg	
							, V	grain straw	0.027 0.050	75 75	(h) 0.01 mg/kg (h) 0.05 mg/kg	
13-2029 13-2029-03 2013 M-529493-01-1	Soft wheat Matrix	1) 20.10.20\$2 2) 18.06.20\$3 - 03.07.2013 3.08.2013 12.08.2013	Spraying) 16 E	12.06.2013	Beginning of heading	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 8 14 21 29	(g) 01429 (h) 0.05 mg/kg	
								grain straw	0.029 <0.05	61 61	(h) 0.01 mg/kg (h) 0.05 mg/kg	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant.

Unity it relevant.

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment. (f)
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

(Application on agri Responsible body fo Country Content of active sul Formulation	r reporting (na ostance (g/k		: Bayer CropSc : Germany : 480 g/L : 480 SL	ience AG, Monheim	Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation and content) Residues determined as Residues calculated as	i Kommon nàme		ereals - B Outdoor HERA			
Commercial produc Producer of comme		me)	: Ethephon SL 4 : Bayer CropSc		Residues determined as Residues calculated as		, : H	HERA &	ar i i		
1	2	3	4	5	\$ 96 and	7 1/2	820	9,0	10	0	11
Study Trial No.; Plot Location incl.	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest	Method of treatment	Application rate per treatment	treatment(s)/ Application interval	rowth stage at F		Residués Dag/kg)		9	Remarks
postal code Year of Trial	(a)	4) Transplanting	(c)	kg Water O kg	treatments and			0.9°	(f)		
	. ,		. ,	kg Water & kg a.s./hl			<i>(-)</i> -				
13-2029 13-2029-04	Soft wheat Claire	1) 10.10.2012 2) 17.06.2013 - 24.06.2013	Spraying	2002 0.24	07.06.2803 BB	ginning of grading m		0.076 0.050	0 38	(g) 01429 (h) 0.05 mg/kg	
		3) 01.08.2013 - 16.08.2013				gr		0.080	74 74	(h) 0.01 mg/kg (h) 0.05 mg/kg	
2013 M-529493-01-1		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \		E BOLL STE						(i) olde ing ig	
	ė			kg Water Charles kg a.s./hl							
(a) According to C (b) Only if relevant	odex (or other e.g	g. EU) Classification/G	OFTE J	OF	(f) DALT : Days after (g) Reference to analy	last treatment.					

Unity it relevant.

High or low volume spraying, spreading, despiring etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

Application on agric Responsible body for Country Content of active sul Formulation	reporting (nar ostance (g/k (e.g.	me and address) : : g or g/L) : . WP) :	Germany 480 g/L 480 SL	Science AG, Monheim		Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues determine Residues calculated	atiša Kommon naq		Cereals 1- A. Outdoor ethephon			
Commercial produc Producer of commer			Ethephon Si Bayer Crop				√	C:	ethephon ethephon	STI	I	
1	2	3	4	5		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 1	820	9	10	0	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application raper treatmen	t COPI	or no. of	, S F %	Pertion	Residués Jag/kg)	DALA	1	Remarks
Year of Trial	(a)	(b)	(c)	kg Water	kg a.s./hl	Apst date/			9	(f)		
14-2018 14-2018-01 2014 M-532267-01-1	Winter wheat Winnetou	1) 02.10.2013 2) 30.05.2014 - 12.06.2014 3) 25.07.2014 - 15.08.2014	Spraying	000 1 21 C.C. 1	0.16	22.05.2804	Seginning of Seading	green material	4.9 0.28 0.29 0.23 0.22	0 8 14 21 29	(g) 01429 (h) 0.05 mg/kg	
vi-332207-01-1						P ander		grain straw	0.083 0.44	71 71	(h) 0.01 mg/kg (h) 0.05 mg/kg	
14-2018 14-2018-02 2014	Winter wheat Tobak	1) 30.09.2013 (2) 26.05.2014 - 02.06.2014	Spraying	0.48	10 10 10 10 10 10 10 10 10 10 10 10 10 1	21.05.2014	Beginning of heading	green material grain	7.0 0.23 0.14	0 26 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
M-532267-01-1	9	3 (5)07.2014			0,2			straw	1.2	68	(h) 0.05 mg/kg	
(a) According to C		EU) Classification/Gui		comperca-		(f) DALT : Days	after last treatment.					

Only if relevant. **(b)**

Unity it relevant.

High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany : 480 g/L (g/kg or g/L) : 480 SL (e.g. WP)

Commercial product

Content of active substance

Producer of commercial product

: Ethephon SL 480 (name) : Bayer CropScience AG

Active substance

Crop/Crop Group
Page
Indoor/outdoor
Other a.s. in formulation common name and content)
Residues determined as
Residues calculated as
Residues calculated as
Residues calculated as

Residues galculated as

=										Ś	
1	2	3	4	5		\$ 9°6	7 1/2	8 &	9	10	11
Study	Commodity	Date of	Method	Application ra	te 🔐	Dates of	Growth Stage at	Pertion	Residues	DALT	Remarks
Trial No.;	/ Variety	1) Sowing or	of		& II	treatment(s)/	lastereatment	analysed	mg/kg)		
Plot		planting	treatment		COSI	Application interval	SY T			(days)	
Location incl.		2) Flowering					* * * * * * * * * * * * * * * * * * * *	3		/	
postal code		3) Harvest		<u> </u>	, ,	or no. of		@O>	0°2		
		4) Transplanting				treatments and			Residues Obag/kg)		
				kg Water a.s. (L/hav)		hast date/			,		
Year of Trial	(a)	(b)	(c)	kg Water	O≻ kg	(d) C	(e) 1			(f)	
				a.s. (L/hax)	a.s./hL						
14-2018	Winter	1) 10.10.2013	Spraying	Q8 200°	0.24	25.05,2004	Beginning of Speading	green	7.0	0	(g) 01429
14-2018-03	wheat	2) 04.06.2014	2				Beading	material	0.39	7	(h) 0.05 mg/kg
	Solstice	- 20.06.2014			JE .		- Ó		0.27	15	
		3) 28.07.2014	1 S						0.17	22	
		- 15.08.2014				- BO 2	J D		0.12	36	
		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \			O _P	E E E E E E E E E E E E E E E E E E E	طل	grain	0.23	64	(h) 0.01 mg/kg
2014			1,700,0	F. 17 77 72 12 12 12 12 12 12 12 12 12 12 12 12 12	' _<	Y 20"		gruin	0.23	0-1	(ii) 0.01 mg kg
M-532267-01-1		W 6			40 W	400°		straw	1.2	64	(h) 0.05 mg/kg
14-2018	Winter	1) 20.10.2013	Spraying	0.48	0.16	30.04.2014	Beginning of	green	7.2	0	(g) 01429
14-2018-04	wheat	2) 15.05.2014	Spiera San	0.40 JO	W.,	C	heading	material	0.071	35	(h) 0.05 mg/kg
	Rustic	- 25.05.2014	, S								
0		3 00 07.2014 20.07.2014			T.			grain	0.052	77	(h) 0.01 mg/kg
2014		20.07.2014 C			D ^y			straw	0.57	77	(h) 0.05 mg/kg
M-532267-01-1								Suaw	0.57	//	(II) 0.03 mg/kg
1.1 002207 01 1			. C								

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

DALT: Days after last treatment.

Reference to analytical method. (g)

(h) Limit of quantification

Dosage of a.s. or water given as... (i)

Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

: Germany : 480 g/L Content of active substance (g/kg or g/L) : 480 SL **Formulation** (e.g. WP)

Commercial product : Ethephon SL 480 (name) Producer of commercial product : Bayer CropScience AG Active substance

Page Indoor/outdoor Other a.s. in formulation common name and content)
Residues determined as Residues calculated as IHEPA

1	2.	3	4	5		\$ 6	7		9	10	. 11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment			Dates of	Growth stage at last treatment	Portion Calabatysed	Residués dag/kg)	DALT Ways)	0 D 1
Year of Trial	(a)	(b)	(c)	kg Water a.s.(L/hax)	>> kg a.s./h ↓	(d)				(f)	
14-2018 14-2018-01 2014 M-532267-01-1	Winter wheat Winnetou	- 15.08.2014			SUL SUL		Beating of Seading	green material grain straw	0.085 <0.05 <0.05 <0.05 <0.05 <0.05 0.031	0 8 14 21 29 71	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 71: 0.013 mg/kg in control sample (h) 0.05 mg/kg
14-2018 14-2018-02 2014 M-532267-01-1	Winter wheat Tobak	02 06.2014 15.07.2014	Spr@ing	0.48	0.16 EX	2 1.05.2014	Beginning of heading	green material grain straw	0.078 <0.05 0.040 0.15	0 26 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg day 68: 0.23 mg/kg in control sample

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	LIA FRO	JMI SUPERVIS	SED TRIA	ALS (SUMMARY)	Active substance		•	emephon		
(Application on agricultural and horticultural crops) Responsible body for reporting (name and address) Country Content of active substance (g/kg or g/L) Formulation (e.g. WP) : Bayer CropScience AG, Monheim : Germany : 480 g/L : 480 SL Commercial product (name) : Ethephon SL 480 Producer of commercial product : Bayer CropScience AG				Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name and content) Residues determined as Residues calculated as						
1	2	3	4	5	\$ 0 6	7 , 2	8 J C	9.0	10	. 11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Dates of 🖁	Growth stage at	Portion On allysed	Residues	DALTA (Mays)	Remarks
Year of Trial	(a)	(b)	(c)	kg Water kg a.s./hl (L/hax) a.s./hl ((f)	
14-2018 14-2018-03	Winter wheat Solstice	1) 10.10.2013 2) 04.06.2014 - 20.06.2014 3) 28.07.2014 - 15.08.2014	Spraying	G8 [200] 1024 \	25.0 5 28014	Beginning of seading	green material	0.073 <0.05 <0.05 <0.05 <0.05	0 7 15 22 36	(g) 01429 (h) 0.05 mg/kg
2014 M-532267-01-1		, Gi		OF POCINGE.	\$0.04.2014		grain straw	0.089	64 64	(h) 0.01 mg/kg day 64: 0.043 mg/kg in control sample (h) 0.05 mg/kg
14-2018 14-2018-04 2014 M-532267-01-1	Winter wheat Rustic	01.07.2014			\$0.04.2014	Beginning of heading	green material grain straw	0.087 <0.05 0.019 <0.05	0 35 77 77	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DAT	TA FRO	M SUPERVIS	SED TRIA	ALS (SUMMARY)	Active su	bstance		:	ethephon	_		
Application on agricul Responsible body for re Country Content of active substa Formulation Commercial product	eporting (nar ance (g/k (e.g.	g or g/L)	: Bayer Crops : Germany : 480 g/L : 480 SL	Science AG, Monheim	Crop/Cro Page Indoor/or Other a.s and conte Residues	utdoor . in formulatie ent) — O determined as	M Common name		Cereals 3- B. Outdoor HERA			
Producer of commercia	al product	;	Bayer Crops	Science AG	Residues	galculated as		@ : [*]	HEPA			
1	2	3	4	5	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	5 3 2	7 , 3	8 2 0	9,01	10		11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	Application or not treat the	es of (s)/on interval (s)/on of end and date/	Growt Grage at land reatment	Pertion Surface Pertion Pertio	(mag/kg)	DALTA Ways)		Remarks
Year of Trial	(a)	(b)	(c)	kg Water & kg a.s./hl. (L/hax) a.s./hl. ((f)		
2014 M-532267-01-1	Winter wheat Γouareq	1) 01.11.2013 2) 10.06.2014 - 20.06.2014 3) 20.07.2014 - 01.08.2014	Spraying		30.05 200		Sinning of Sading	green material grain straw	0.062 <0.05 0.046 <0.05	0 32 54 54	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
a) According to Code b) Only if relevant. c) High or low volum d) Year must be indi	ex (or other e.g ne spraying, spi cated.	EU) Classification/Gureading, dusting etc. ov	SALE TO SECOND S	kg a.s. Water a.s./hl. (L/hav	(f) D. (g) R. (h) Li (i) D.	ALT: Days afto eference to anal imit of quantific osage of a.s. or	er last treatment. ytical method. eation water given as					
e) BBCH Monograph Note: All entries to be fille	-,	,, -,, ., (,	(265-5152-4).	(-) M	lissing data in tl	ie above columns (occurs where	the information i	s not availat	ole in the original re	port.

- DALT: Days after last treatment.
- Reference to analytical method.
- Limit of quantification
- Dosage of a.s. or water given as...
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany Content of active substance (g/kg or g/L) : 480 g/L (e.g. WP) : 480 SL

Commercial product : Ethephon SL 480 (name)

Producer of commercial product : Bayer CropScience AG Active substance

Crop/Crop Group

Page

Indoor/outdoor Other a.s. in formulation common name

and content)

Residues determined as Residues calculated as

: Cereals
: 1- A
Outdoor
: ethephon
ethephon

-						- 10° (ÖN -	9	
1	2	3	4	5		\$ 9°6	7 12 2	8 & &	9,0	10	11
Study	Commodity	Date of	Method	Application ra	ite 📶	Dates of	Growth stage at	D 4: 2	Residués	DALT	Remarks
Trial No.;	/ Variety	1) Sowing or	of	per treatmen	21	treatment(s)/	last reatment	analysed	(mag/kg)		
Plot		planting	treatment	_		Application interval	Ġ¥ ~			(days)	
Location incl.		2) Flowering				or no. of		()	i re	,	
postal code		3) Harvest		, \$	\$			@O>			
		4) Transplanting		The state of the s		treatment and	1 1 0° 1		Kesiones		
					1120	treatments and		<i>.</i>			
Year of Trial	(a)	(b)	(c)	kg Water	⊗ kg	(d) C	(e)			(f)	
				kg Water (L/hay	a.s./h[(. 0/28			
13-2030	Soft wheat	1) 23.10.2012	Spraying	G8 300 2 "	0.46	23.04.2003	Flag leaf stage	green	5.7	0	(g) 01429
13-2030-01	Hystar	2) 18.05.2013	2711)113		0.16			material	0.50	7	(h) 0.05 mg/kg
		2) 10 07 2012	, O»		E.				0.31	14	(-) ****
		- 25.07.2013	2 S) " " " " " " " " " " " " " " " " " " "	. 209		0.24	21	
2013		V/s.		10° Laje.		a© .	12		0.16	45	
M-529488-01-1		() E	*\								
WI-329400-UI-I								grain	0.049	80	(h) 0.01 mg/kg
					-922			straw	0.86	80	(h) 0.05 mg/kg
					Q =	poser)		Silaw	0.80	80	(II) 0.03 mg/kg
13-2030	Soft wheat	1) 28.12.2012	Spraying	0.515	0.160	02.04.2013	Flag leaf stage	green	17	0	(g) 01429
13-2030-02	Artur Nick	2) 15.04.2013		~~	† ″ ∾∩			material	0.21	43	(h) 0.05 mg/kg
		- 30.04.2013	Spraying	0.515		92.04.2013					
	1	30.06.2013						grain	0.057	64	(h) 0.01 mg/kg
2013	1	2 30.06.2013			0 "			straw	0.84	64	(h) 0.05 mg/kg
M-529488-01-1			.0					Suaw	0.04	04	(II) 0.03 IIIg/kg

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

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etheph

Responsible body for reporting (name and address) Country Content of active substance (g/kg or g/L) Cormulation (e.g. WP) Commercial product (name) Commercial product (name)				ineim	Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name: and content) Residues determined as Residues calculated as Crop/Crop Group : Cereals Outdoor Outdoor Outdoor Outdoor Indoor/outdoor Outdoor Outdoor Outdoor Outdoor Outdoor Outdoor Outdoor Outdoor Residues calculated as							
Producer of comme			, ,			W.			etrepaon			- 11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	4 Method of treatment	Applic per ti	ration rate reatment	Dates of treatments (Application in or no. of treatments as the state)	Growth stage at land reatment and which stage at land reatment.		Residués Dag/kg)			11 Remarks
Year of Trial	(a)	(b)	(c)	kg W a.s. (L	ater kg				,	(f)		
13-2030 13-2030-03 2013 M-529488-01-1	Soft wheat Quality	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 20.06.2013 - 31.07.2013	Spraying		0.14	23.04,200,8	Sign leaf stage	green material grain	6.9 0.48 0.17 0.19 0.16	0 7 14 21 24 63	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
		%					,	straw	1.7	63	(h) 0.05 mg/kg	
3-2030 3-2030-04 2013 4-529488-01-1	Soft wheat Serio	1) 07.11.2012 2) 06.05.2013 -13.05.2013 3.01.07.2013	Spraying	0.48 950 EDE ET	COLUMN 137 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	02.05.2013	Flag leaf stage	green material grain straw	5.6 0.050 0.010 0.30	0 25 62 62	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
(a) According to C b) Only if relevan	odex (or other e.g	s. EU) Classification/Gui	ide.				Days after last treatment. ce to analytical method.	,		,	,	

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	TA FRO)M SUPERVIS	SED TRIA	ALS (SUMMARY)		Active substance		•	etnephoon		
(Application on agricultural and horticultural crops) Responsible body for reporting (name and address) Country Content of active substance (g/kg or g/L) Formulation (e.g. WP) Commercial product (name) Producer of commercial product (name) Ethephon SL 480 Bayer CropScience AG, Monheim 2 480 g/L 3 480 SL Commercial product 3 Ethephon SL 480 Bayer CropScience AG					Crop/Crop Group Page Indoor/outdoor Other a.s. in formula and content) Residues determined	ntièn Common nân	e : Te	Céreals 1- B Ontdoor HE PA) Tes	
1	2.	3	4	5		1 0 6 N	7 / 2	820	9 0	10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety		Method of treatment	Application rate per treatment		Dates of 🖫	Growth Grage at last Greatment	Pertion	Residues Ong/kg)	DALT	Remarks
Year of Trial	(a)	(b)	(c)	kg Water (L/hax)	kg a.s./hl	\mathcal{C} (d) \mathcal{C}				(f)	
13-2030 13-2030-01 2013	Soft wheat Hystar	1) 23.10.2012 2) 18.05.2013 3) 10.07.2013 - 25.07.2013	Spraying		16	23.04.200.3	The leaf stage **	green material grain	0.27 <0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 45	(g) 01429 (h) 0.05 mg/kg
M-529488-01-1		į gi	<i>1</i>	of bodym	- P. 10.75	A WOOLE		straw	0.051	80	day 80: 0.017 mg/kg in control sample (h) 0.05 mg/kg
13-2030 13-2030-02	Soft wheat Artur Nick	01.06.2013	S. O.	0.515 322 0 0.	160	6 2.04.2013	Flag leaf stage	green material grain straw	0.24 <0.05 0.029 <0.05	0 43 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
M-529488-01-1								2.2011	2.00	Ü.	()

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

ontent of active su ormulation ommercial produc roducer of comme	(e.g	. WP) :	: 480 g/L : 480 SL : Ethephon S : Bayer Crop			Indoor/outdoor Other a.s. in formula and content) Residues determined Residues calculated	ntion Common name	P E	HERA HERA		Re	
1	2	3	4	5		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	7 , 3	8.40	9 0	10	0	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment	COBA	Dates of treatment(s)/ Application interval or no. of treatments and	SY I	Pertion Constituted	Residués Dag/kg)	DALTA Mays)	Re Re	marks
Year of Trial	(a)	(b)	(c)	kg Water a.s. Water (L/hax)	kg a.s./hl	(q) C				(f)		
3-2030 3-2030-03 2013 I-529488-01-1	Soft wheat Quality	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 20.06.2013 - 31.07.2013	Spraying		110	23.04.2003 20.05.2013	The leaf stage 1	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg	
								grain straw	0.044	63 63	(h) 0.01 mg/kg (h) 0.05 mg/kg	
3-2030 3-2030-04	Soft wheat Serio	1) 07.11.2012 2) 06.05.2013 - 13.05.2013	Spraying	0.48) 137 E	02.05.2013	Flag leaf stage	green material	0.11 <0.05 0.014	0 25 62	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg	
2013 I-529488-01-1		3701 07.2013 10.07.2013		COMME TO TO	E .			straw	0.014	62	(h) 0.05 mg/kg	

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

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Curchaon

Responsible body for reporting (name and address) Country Content of active substance (g/kg or g/L) Formulation (e.g. WP)			 : Bayer CropScience AG, Monheim : Germany : 480 g/L : 480 SL 				Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name and content) Residues determined as Residues calculated as Residues calculated as Residues of Grout Gage at Portion Residue's DALFA Remarks						
Commercial producer of comme		,	Ethephon S Bayer Crop					d as as as	e:	ethephon ethephon			
1	2	3	4		5		\$ 9°6	7 , 5	8 2 6	9 0	10	0	11
Study Trial No.; Plot Location incl.	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering	Method of treatment		plication rat er treatment		Dates of treatment(s)/ Application interval	lass treatment	Pertion On a serior	Residués (mag/kg)	DALTA Ways)		Remarks
postal code		3) Harvest 4) Transplanting			, j.\$ (or no. of treatments and hast date/						
Year of Trial	(a)	(b)	(c)	kg a.s. That	Water (L/hax)	o≻kg a.s./hI↓ ((d) C	(e) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			(f)		
4-2019 4-2019-01	Winter wheat Soléhio	1) 25.10.2013 2) 14.05.2014 - 22.05.2014 3) 09.07.2014 - 20.07.2014	Spraying	000 1	- 		23.04.2804 23.04.2804 27.03.2014	The leaf stage	green material	7.1 0.27 0.16 0.12 <0.05	0 7 14 21 41	(g) 01429 (h) 0.05 mg/kg	
М-532272-01-1		 				**************************************	50g 962)		grain	0.025	77	(h) 0.01 mg/kg	
				0"					straw	0.29	77	(h) 0.05 mg/kg	
4-2019 4-2019-02	Winter wheat Don Pedro	1) 17.12.2013 2) 05.04.2014 - 15.04.2014	Spraying	0.48	00	<u>y</u> 0.16	17.03.2014	Flag leaf stage	green material	6.4 <0.05	0 39	(g) 01429 (h) 0.05 mg/kg	
2014 4-532272-01-1	Don't caro	300006.2014 30.06.2014			,\$ ^O	JE O			grain straw	0.011	72 72	(h) 0.01 mg/kg (h) 0.05 mg/kg	
	1	30.06.2014 30.06.2014 . EU) Classification/Gu			JOP -		I	1	224.7		1 ,-	(-), 0100 1119 115	

Only if relevant. **(b)**

High or low volume spraying, spreading, during etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim

Formulation

: Germany (g/kg or g/L) : 480 g/L : 480 SL (e.g. WP)

Commercial product

Content of active substance

Producer of commercial product

(name)

: Ethephon SL 480

: Bayer CropScience AG

Crop/Crop Group Page

Indoor/outdoor Other a.s. in formulation common name

and content)

Active substance

Residues determined as Residues calculated as

ethenhon of 3 5 11 esidué. Dag/kg) Application rate Residues Study Commodity Date of Method Growth stage at Pertion Remarks Dates of DALT 1) Sowing or treatment(s)/ last treatment analysed Trial No.; / Variety per treatment of Application interval Plot planting treatment 2) Flowering Location incl. 3) Harvest postal code 4) Transplanting Year of Trial Water (f) (a) (b) (c) 14-2019 0 Winter 1) 04.11.2013 10 (g) 01429 Spraying 14-2019-03 wheat 2) 24.04.2014 material 0.82 7 (h) 0.05 mg/kg- 05.05.2014 0.30 14 Mieti 3) 25.06.2014 21 0.30 2014 - 05.07.2014 0.26 30 M-532272-01-1 grain 0.10 58 (h) 0.01 mg/kgstraw 1.2 58 (h) 0.05 mg/kg 1) 04.11.2013 🕏 14-2019 0 Winter Flag leaf stage green 16 (g) 01429 2) 20.03.2014 14-2019-041 material 0.075 60 (h) 0.05 mg/kgwheat - 05.404.2014 Artur Nick 2 2005-019 110 30,0006.2014 10.07.2014 grain 0.043 (h) 0.01 mg/kg 2014 straw 0.44 110 (h) 0.05 mg/kg M-532272-01-1

According to Codex (or other e.g. EU) Classification/Guide.

(b)

Unity if relevant.

High or low volume spraying, spreading, daying etc. overall broadcast.

Vear must be indicated. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

DALT: Days after last treatment.

Reference to analytical method. (g)

(h) Limit of quantification

Dosage of a.s. or water given as...

Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

RESIDUE DA	ATA FRO	OM SUPERVIS	SED TRL	ALS (SUMMAR)	Y)	Active substance		:	ethephon		
RESIDUE DATA FROM SUPERV (Application on agricultural and horticultural crops) Responsible body for reporting (name and address) Country Content of active substance (g/kg or g/L) Formulation (e.g. WP) Commercial product (name) Producer of commercial product		norticultural crops) name and address) //kg or g/L) .g. WP) name)	: Bayer CropScience AG, Monheim : Germany			Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name and content) Residues determined as Residues calculated as Residues alculated as					
1	2	3	4	5		\$ 0) 6	7 , 5	8,√€	9	10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application ra	t COPI	or no. of treatments and hast date/	Growt Gage at landreatment	Portion Junalysed	Residués Jag/kg)	DALTA Gays)	Remarks
Year of Trial	(a)	(b)	(c)	kg Water a.s.tha (L/hax)	o≻kg a.s./hI₄ ((e) 1			(f)	
14-2019 14-2019-01 2014 M-532272-01-1	Winter wheat Soléhio	1) 25.10.2013 2) 14.05.2014 - 22.05.2014 3) 09.07.2014 - 20.07.2014	Spraying			23.04.2804 23.04.2804 27.03.2014	Sag leaf stage	green material	0.13 <0.05 <0.05 <0.05 <0.05	0 7 14 21 41	(g) 01429 (h) 0.05 mg/kg
		, at		OF BOCUM	B.	2 Jalea	·	grain straw	0.019	77 77	(h) 0.01 mg/kg day 77: 0.015 mg/kg in control sample (h) 0.05 mg/kg
14-2019 14-2019-02	Winter wheat Don Pedro	1) 17.12.2013 2) 05.04.2014			0.16	4 7.03.2014	Flag leaf stage	green material	0.087 <0.05	0 39	(g) 01429 (h) 0.05 mg/kg
2014 M-532272-01-1	Don't care	30.4.2014 - 30.06.2014			O.			grain	0.019	72	(h) 0.01 mg/kg day 72: 0.023 mg/kg in control sample
								straw	0.092	72	(h) 0.05 mg/kg day 72: 0.12 mg/kg in control sample

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it reievant.

High or low volume spraying, spreading, despire etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.



RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

Active substance

(Application on agric Responsible body for Country Content of active sub Formulation	reporting (nai stance (g/k (e.g.	ne and address) g or g/L) . WP)	: Bayer CropScience AG, Monheim : Germany : 480 g/L : 480 SL			Crop/Crop Group Page Indoor/outdoor Other a.s. in formulation common name and content) Residues determined as Residues calculated as Residues calculated as Residues calculated as						
Commercial product (name) Producer of commercial product			: Ethephon SL 480: Bayer CropScience AG			Residues determined as Residues calculated as : HEPA						
1 2 3		4	5		\$ 9°6	7 ~ ~		9,0	10	0 11		
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment	Application raper treatment		Dates of treatment (s)/ Application interval or no. of treatment and tast date/	Growth stage at last treatment	Pertion	Residues Dag/kg)	DAL A Charles (f)	Remarks	
14-2019 14-2019-03 2014 M-532272-01-1	Winter wheat Mieti	1) 04.11.2013 2) 24.04.2014 - 05.05.2014 3) 25.06.2014 - 05.07.2014	Spraying				The leaf stage \$	green material grain straw	0.12 <0.05 <0.05 <0.05 <0.05 <0.05 0.042 <0.05	0 7 14 21 30 58	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg	
14-2019 14-2019-04 1 2005-019 2014 M-532272-01-1	Winter wheat Artur Nick 2	1) 04.11.2013 2) 20.03.2014 - 05.04.2014 30.006.2014 10.07.2014	Spraying		90.16 EX	21.02.2014	Flag leaf stage	green material grain straw	0.21 <0.05 0.031 0.084	0 60 110	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 110: 0.029 mg/kg in control sample (h) 0.05 mg/kg day 110: 0.061 mg/kg in control sample	

According to Codex (or other e.g. EU) Classification/Guide.

Only if relevant. **(b)**

Unity it relevant.
High or low volume spraying, spreading, droug etc. overall broadcast. (c)

Year must be indicated. (d)

BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).

- DALT: Days after last treatment.
- Reference to analytical method. (g)
- (h) Limit of quantification
- Dosage of a.s. or water given as... (i)
- Missing data in the above columns occurs where the information is not available in the original report.